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OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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CONTENTS:

Correction - - - - - - - - - - - - - - 59

Candidates for the 1953 Election - - - - - - - 60

Statistical Methods Applied to the Analysis and Testing of Leather *By* R. M. LOLLAR - - - - - 60

Study of the Burst Test as Applied to Military Upper Leather *By* E. B. RANDALL, C. W. MANN, J. R. KANAGY and J. W. MANDEL - - - - - - - - - - - 84

Use of Carbon Dioxide for Deliming *By* E. E. OCHS - - 105

Abstracts - - - - - - - - - - - - - - 110

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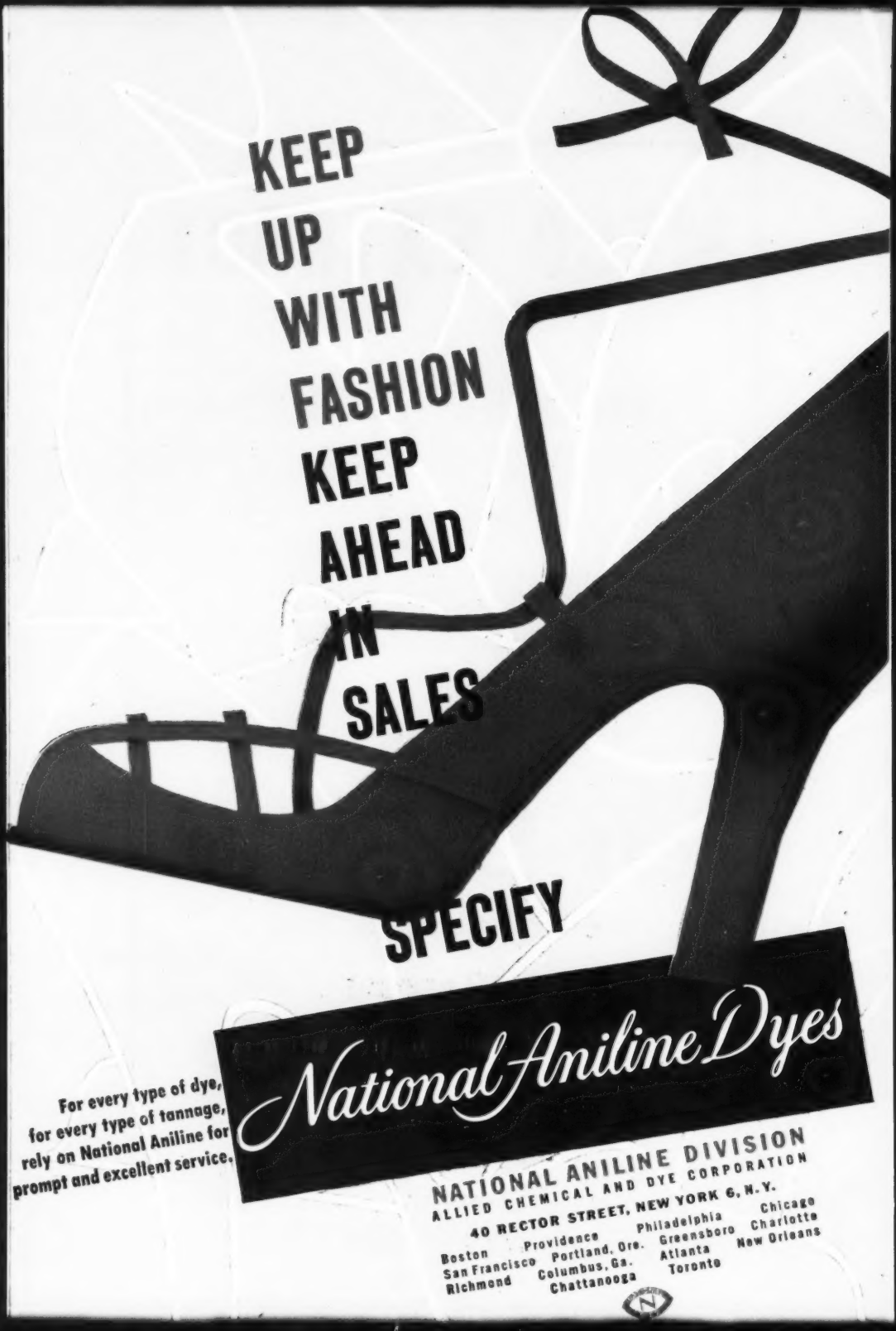
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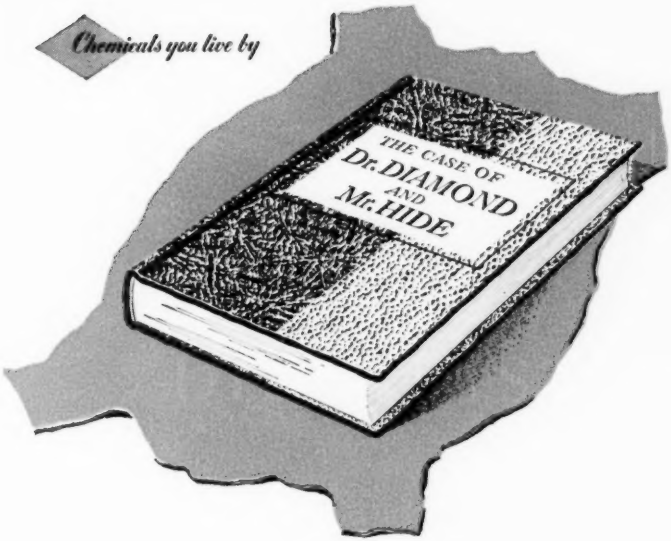

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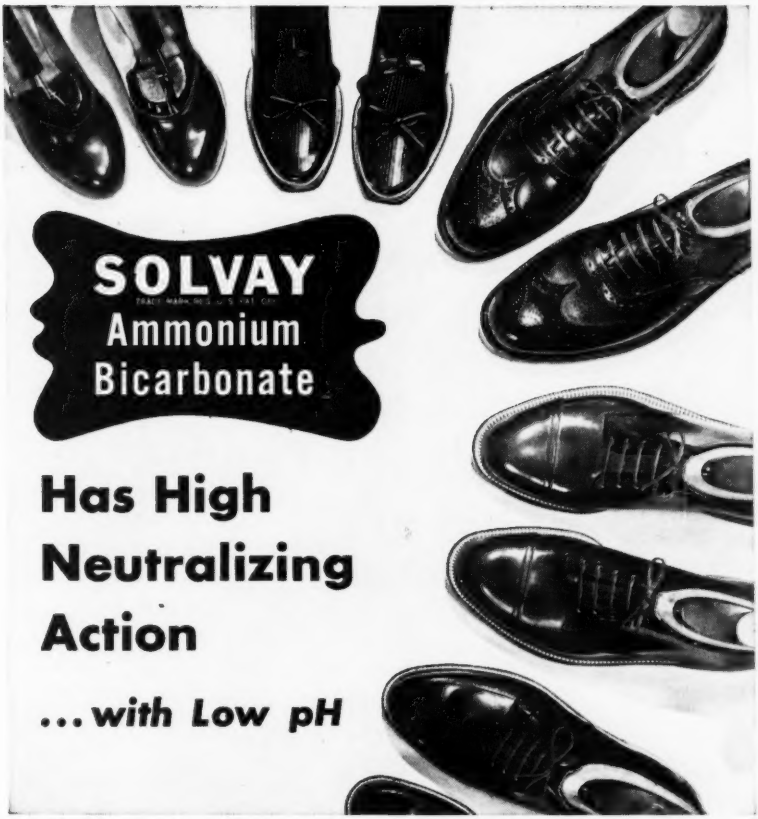

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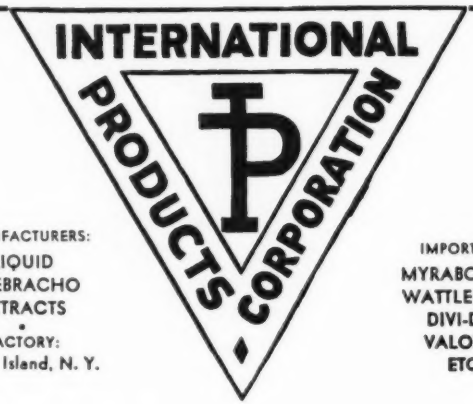

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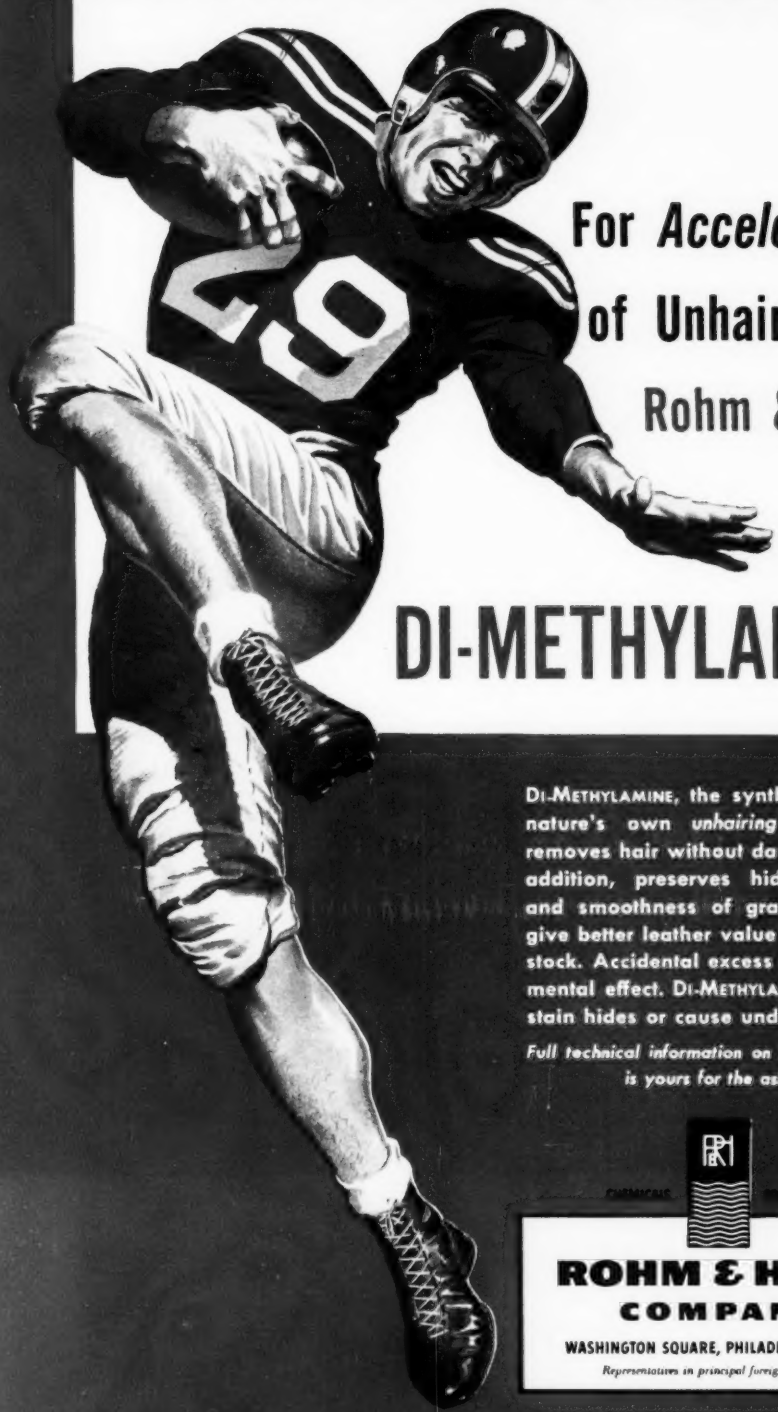

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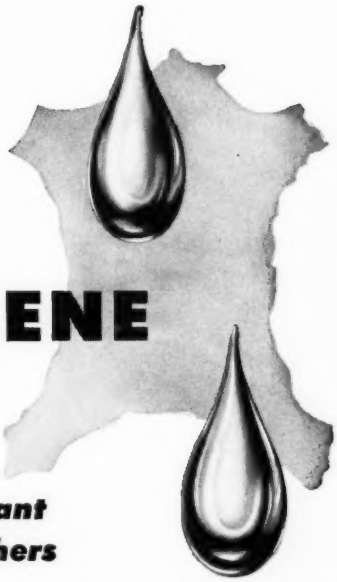

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CORRECTION

K. H. Gustavson has noted the following corrections to be made in his paper "Physico-Chemical Studies of Extremely Basic Chromic Chlorides" which appeared in the March 1952 Journal.

Line 20 from the top of page 159, read "uncharged" instead of "unchanged".

Line 6 from the bottom of page 161, read "fixation of complexes" instead of "fixation or complexes".

Line 8 from the top of page 162, read "30 per cent" instead of "3 per cent" and line 6 from the bottom of page 162, read "McBain" instead of "McVain".

CANDIDATES FOR THE 1953 ELECTION

Candidates for Council:

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JOSEPH R. KANAGY
J. STANLEY KIRK
THOMAS C. THORSTENSEN
HARRY R. WILSON

The above slate of candidates has been prepared by the Nominating Committee.

AL FLEISH
DAVE WILSON
ROBERT ADAMS, *Chairman.*

Members Note:

Article V - 2, Nominations (c)

Additional candidates may be nominated by petitions, signed by 15 or more active members. Such petitions shall reach the Secretary not later than April 1st, and shall contain a statement of the willingness of the nominee to serve if elected. No member shall sign more than one petition for each office to be filled.

Statistical Methods Applied to the Analysis and Testing of Leather*

By ROBERT M. LOLLAR

Department of Basic Science in Tanning Research
Foundation Tanners' Council of America
University of Cincinnati
Cincinnati 21, *Ohio*

Statistical experimental methods are receiving increasing use by chemists. Evidence for this is seen in the American Chemical Society symposium on the statistical design of experiments for the development of new analytical methods [1], and the symposium of the New York Academy of Science on the place of statistical methods in biological and chemical experimentation [10]. Other technical associations have been very active in the application of statistical methods to the problems of analysis and testing. The American Society for the Testing of Materials has prepared a manual on the quality control of materials [3] which will be very informative to the chemist who desires a non-mathematical presentation of the basic fundamentals of the

*Preliminary reports upon this subject have been made to the American Leather Chemists Association through papers at its annual meetings and reports to its Technical Committees during the period from 1950 to 1952.

statistical approach to sampling and process control. This booklet is concerned with the techniques of statistical quality control whose applicability to problems of the leather industry has been discussed by Cox [8].

The use of statistical methods in leather chemistry is not new. Spiers [23] discusses sampling of leather from a statistical viewpoint, while McKay [18] examined the chemical and physical properties of sole leather with especial emphasis of the statistical validity of his conclusions. Beek [4] showed that the probable error of a single measurement of the tensile strength of vegetable tanned heavy leather was 265 lb. per sq. in. He specifically notes that this value does not include the variation due to the area of the hide, the hide to hide variations, or the tannery to tannery variation. Beek and Hobbs [5] applied these and other data on the tensile strength of vegetable tanned heavy leather to develop a sampling schedule for the leather. Emley [11] has noted how this information and practical considerations relative to cost lead to the decision that no less than 7 nor more than 20 individual pieces should be tested on any lot of leather. Federal Specification KK-L-311 has adopted this decision as the basis of its method of sampling, and seven has become almost the magic number for leather chemists as well as for crap shooters.

The fire resistance sub-committee of the American Leather Chemists' Association physical testing committee has published [12] the results of their development of new methods for the evaluation of the fire resistance of leather, which methods development work was evaluated by the use of statistical methods. Mitton [19] has described the statistical approach to the planning and interpretation of experiments on a variable material such as leather. Mitton and his associates have reported on the applications of statistical methods in research studies on the effect of mold growth on vegetable tanned leather [22], on the effect of tannage under tension on the tensile strength of leather [21], and on the effect of humectants on the extensibility of the grain of shoe upper leather [20]. Clark and Steiner [6] have reported an informative statistical study of the correlation between the properties of sheepskin leathers tanned with Sicilian and American sumacs. Mann, et al., [17], have noted the variable efficiency of the several areas in the side with reference to the ability of these position averages to predict the lot average of the characteristics of retan leather. This is an application of the work of Mandel and Mann [16] on a statistical solution of a problem arising in the sampling of leather.

Despite these as well as other applications of the techniques of mathematical statistics to the problems of testing and research in the leather industry, there is no systematic record of the inherent errors which would be expected when the standard testing techniques are applied to leather. This information is fundamental to much of our work, whether our interests are in research or in the practical production of leather. This article will present some data

on the inherent variability which has been found when standard analytical techniques are applied to retan leather; furthermore, an attempt will be made to describe some of the fundamental assumptions and techniques of the statistical approach to the problem so that they will be more readily understood by the leather chemist who is not familiar with mathematical statistics.

The Normal Distribution of Measurements

The leather chemist has long known that any measurement he makes of a characteristic of a leather is subject to variation whenever the measurement is repeated. He is all too well aware of the variation in the chemical and physical characteristics of leather from grain to flesh at a given spot in the leather, from position to position within a given side of leather, and from side to side within a given tannery's production of a particular type of leather. Further, he is aware that the different tanneries produce leathers with differences in characteristics even when they are operated by the same management and are endeavoring to produce the same type of leather. However, the leather chemist often does not realize that this variability in characteristics is not unique to the leather industry and he may not realize that the variation which he encounters follows a normal pattern.

Study of the pattern of variation of measurement values in many fields has shown that the normal frequency distribution of measurement data is of the form shown in the top of Figure 1. This distribution is characterized by the following salient form determinants:

a–A central tendency, denoted in the Figure as M, the arithmetic average.

b–A tailing off of the curve in either direction from this central tendency. The vertical axis, scaled as the normal ordinate, gives the probability of securing any given measurement value.

c–The horizontal axis is scaled in terms of multiples of the standard deviation of the frequency distribution, standard deviation, being a measure of the spread of the measurement data.

It will be noted that the normal distribution predicts a very large overall range in the data, and further that it predicts that the probability of the extremes is much lower than that of values near the central tendency. In fact, it has been found that the range limited by plus and minus one standard deviation includes 68.26 per cent of all of the data in a normal population, plus and minus two standard deviations includes 95.56 per cent of all of the values, and plus and minus three standard deviations includes 99.73 per cent of all of the values. In other words, on the average, only 27 individual measurement values out of 10,000 such values taken from a normal population should differ from the arithmetic mean by more than three times the standard deviation.

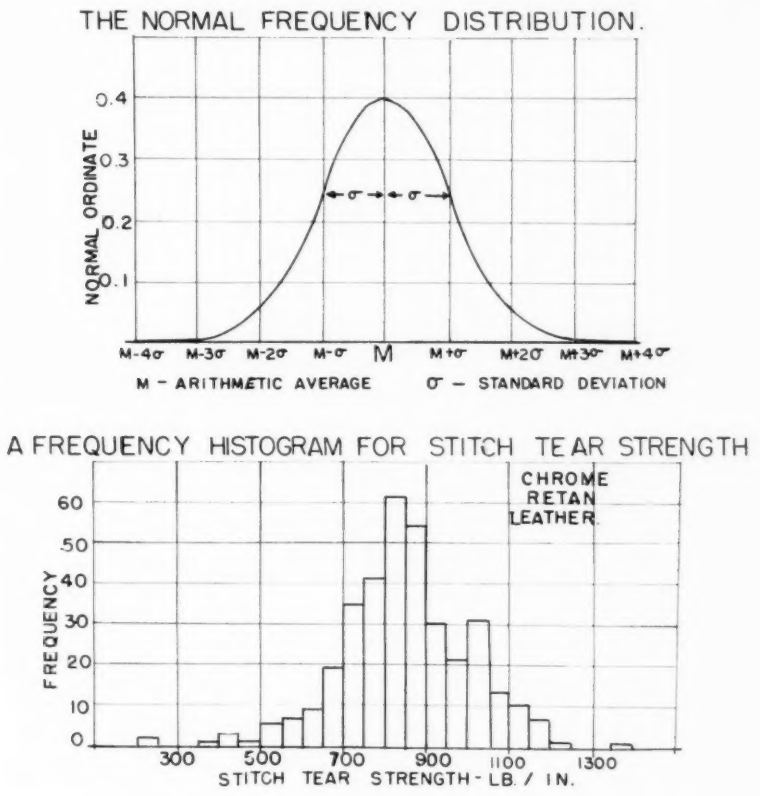

FIGURE 1

How does this apply to measurement data on leather? The lower half of Figure 1 shows the experimental frequency histogram for stitch tear measurements on 350 different sides of chrome retan army shoe upper leather. These sides were sampled near the root of the tail and subjected to the stitch tear procedure specified in Federal Specification KK-L-311, method 246.2. The results are reported in units of lb. per inch obtained when the pounds of load required to tear out the stitch is divided by the thickness of the leather in inches. The data were grouped in intervals covering a range of 50 lb. per inch, and the number of sides having stitch tear values in the several intervals recorded. The number of samples having tear strengths within the intervals are the heights of the bars which have been erected upon the intervals as bases.

It will be noted that the frequency histogram for the stitch tear of retan leather shows a remarkable similarity to the normal frequency distribution. It is noted that there is a central tendency with a maximum frequency of occurence; further, the extremely weak or extremely strong specimens occurred only infrequently. One exception is noted in the high frequency for specimens whose stitch tear value lie between 1000 and 1049. These 350 sides were tanned as a part of the Office of Quartermaster General's program to establish the influence of differences in the levels of vegetable retannage, chrome oxide, and grease content of Army shoe upper leather on the physical properties of the leather. Zacharias, Mann, Steiner, and Horkowitz [2,4] have noted that an increase in the retannage level results in a decrease in the physical strength of the leather. Closer inspection of the data in the frequency histogram revealed that the stitch tear values peaking at 1025 pounds per inch reflect mainly the samples from a 20 per cent retannage level, while those samples whose stitch tear strength shows a maximum around 850 pounds per inch reflect the sides receiving the 40 and 60 per cent retannage level. Thus, this simple graphical technique has shown an assignable source of variability which has also been revealed by the more precise analysis of variance technique [9].

A more precise illustration that strength data from leather exhibit the characteristic frequency distribution can be secured if the data are presented on arithmetic probability paper (Codex No. 3227). This paper shows on its X-axis any specific measured value, for example any strength characteristic of leather. The Y-axis is the percentage of the total number of measured values which lie below any particular strength value. If the normal frequency distribution is exhibited, the resultant graph will show a linear relationship between the cumulative frequency percentage and the strength values. Figure 2 illustrates this relationship. Data were available on almost 1000 sides of retan leather from almost every tanner of this leather. It had been produced during the winter of 1950–1951 to meet Military Specification MIL-L-3122 for chrome retan Army shoe upper leather. The upper curve shows the frequency distribution of the stitch tear strength of this leather expressed in pounds to tear. The samples had been taken from the "A" position of the side, and it is obvious that, between the limits of 2 and 99 per cent of the values, the normal frequency distribution is followed.

Figure 2 also shows the frequency distribution of the load to tear expressed in pounds for the 360 sides of retan leather produced from the several experimental tannages. These are the same sides whose stitch tear strength expressed in pounds per inch was given in the bottom of Figure 1. It will be noted that the distribution is linear, so that the compliance of the data to the normal law is again noted. However, the leather is somewhat stronger than the leather represented by the 980 sides taken from commercial production. This reflects the higher frequency of stronger specimens which caused the frequency histogram in Table I to be bimodal.

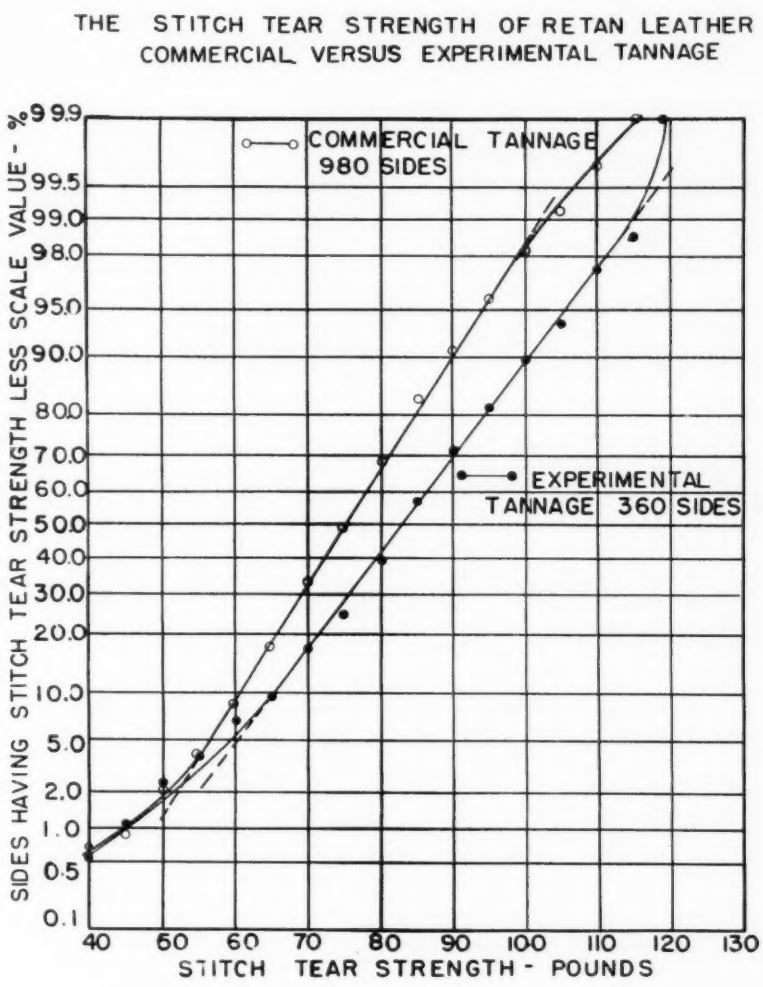

FIGURE 2

As a result of a cooperative project to study the reproducibility of the analyses required to check compliance of retan leather with Federal Specification MIL-L-3122, data were available on the stitch tear strength of 120 sides of retan from each of four tanners. Kidney or "A" position samples had been removed from two sides of their normal production of this leather on each of five working days of twelve consecutive weeks. Thus, the samples taken

should represent the production of these four tanneries within the sampling period, except for any sampling error due to the rather small sample size. Figure 3 demonstrates that the samples of leather from these four tanneries show the normal frequency distribution for their stitch tear strengths, except that the stronger samples are more frequent than would be expected. Further, these four tanners produce leathers that are very similar in stitch tear strength distribution to that shown in Figure 2 for the larger group of samples from

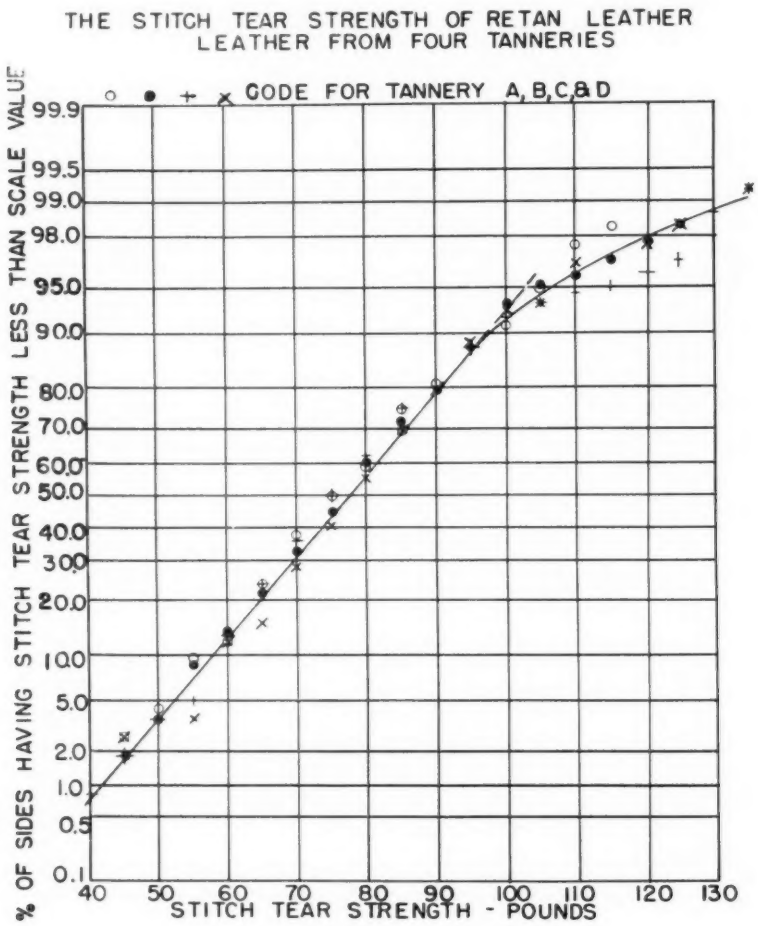

FIGURE 3

several tanneries, except that the four tanneries have more of their leather whose stitch tear strength is greater than 100 pounds.

Figures 2 and 3 demonstrate that the stitch tear strength of chrome vegetable retan military shoe upper leather obeys the requirements for a normal frequency distribution except that the very weak or the very strong samples do not occur at the expected frequency. This failure to follow the normal law at the extremes may well be due to the failure of the relatively small samples which have been examined to accurately reflect the frequency of extremely strong or weak samples in this leather. The variation in the chemical composition and methods of production represented by these leathers is as great as would be expected for this leather. The similarity in the stitch tear strength distribution for all of these leathers is so similar that it suggests that the variability in this type of leather with regard to its stitch tear strength is primarily a reflection of the inherent variability of the hides used to make the leather rather than a reflection of the tannage processes. (Of course, the effect which we noted earlier of a negative correlation between the degree of retannage and the stitch tear is large enough to have a statistically significant influence.)

Figure 4 shows a similar cumulative frequency distribution graph for the load to crack the grain, expressed in pounds as determined on the Mullen tester. One tanner of this leather furnished us the data for 1660 sides of his leather taken over a several months period. It forms the lower of the two curves in Figure 4, from which it will be evident that 90 per cent of the data follow the normal curve, with the deviations again occurring at the extremes. This frequency distribution pattern is partially confirmed by a frequency distribution curve secured in our own laboratory on 274 sides from the majority of the tanners producing chrome vegetable retanned leather during this same period. Unfortunately, in our records those sides cracking at over 850 lb. were merely recorded as exceeding 850 lb., hence the complete curve can not be given. It again seems evident that the primary source of this variability is the inherent variability of the hides. However, it may be noted that first in a four tannery statistical sampling experiment and again in a seven tannery similar experiment, the one tannery which burned the hair off of the hides with sulfide had a statistically weaker grain as revealed by the load to crack on the Mullen tester. This extended over a three months period each time, and was separated by an interval of about six months between the two experiments. Hence, it might be concluded that it seems probable that removal of hair by burning does produce a statistically significant decrease in the grain strength. However, all the leathers exceeded the specification requirements on grain crack.

These examples have been emphasized to demonstrate that the properties of leather do follow the normal frequency distribution law, so that statistical sampling techniques are valid means of securing information about the

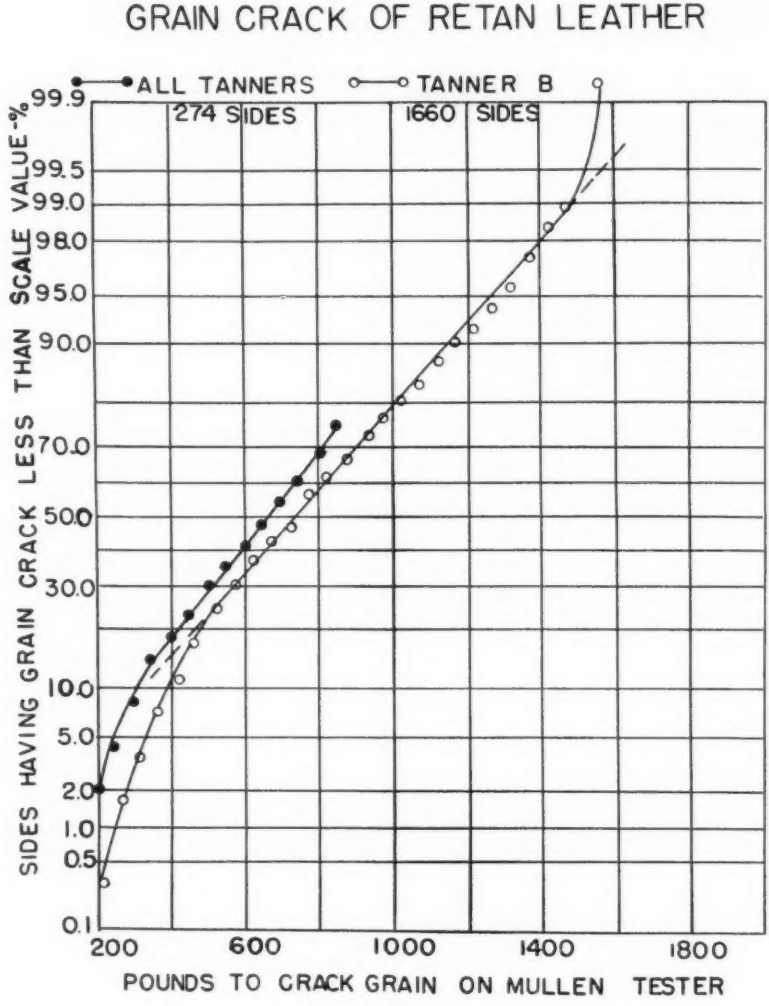

FIGURE 4

properties of a leather. The normal statistical procedures can be applied best where the normal law is observed, although in many cases successful use of statistical methods has been made where the deviation from normality is much greater than we have observed on leather. It may therefore be said with a high degree of confidence that a valid statistical sampling plan can be

designed for use on leather. The design of such sampling plans requires a knowledge of the variability which is inherent in any property which we may wish to measure. Through collaboration with industry, we have been able to secure some data on the inherent variability to be expected when some common methods of analysis are applied to leather. The next section of this paper will summarize the results of this collaborative work.

Experiments in the Statistical Sampling of Retan Leather

Two sampling and testing experiments were conducted upon chrome vegetable retan military shoe upper leather of the type covered by military specification MIL-L-3122, dated 25 January, 1950. The first of these experiments involved the cooperation of four tanneries and four laboratories during a twelve week period early in 1951. The second experiment involved the cooperation of seven tanneries and seven laboratories during a ten week period in the fall of the same year. The tanneries and laboratories of the International Shoe Company, the Pfister and Vogel Tanning Co., the Fred Rueping Leather Co., the tanneries only of the S. B. Foot Tanning Co., and the Northwestern Leather Co., as well as the laboratories only of the leather section of the National Bureau of Standards, the Philadelphia Quartermaster Depot Acceptance Laboratory and the Tanners' Council Research Laboratory were involved in these experiments. Therefore, while all interpretations given in this article are the author's responsibility, they are the result of the work of many individuals in several organizations whose cooperation made this article possible.

The plan of the two experiments required each tannery to select random specimens from each day's production of leather of the type under study, composite them into periodic samples, and ship these samples to the Tanners' Council Research Laboratory. The specimens were then prepared for analysis under the author's supervision. The individual test specimens were then distributed to the cooperating laboratories under a code number. The results were reported to the author for statistical study and interpretation. It should be emphasized that none of the laboratories, including the group at the Tanners' Council Laboratory, had any knowledge of the source of the samples they were examining, so that bias was not introduced into the results.

The experiments were designed as balanced incomplete block experimental designs[7] to minimize the amount of chemical analysis required in a single laboratory testing period. Further, replications were secured by continuing the work over several testing periods in each experiment. The data secured are very voluminous; it is impossible to record all of the original data in this article. Appropriate statistical analyses were made of the data secured to yield an estimate of the error variance to be anticipated from the several analyses required to check compliance of leather with Military Specification

TABLE I

Table of Analysis of Variance for Retan Analytical Data
Tabular Values are Mean Square Values

Variance Source	Degrees of Freedom	Moisture As Is Basis	Grease Analyses As Is Basis	Grease Analyses Dry Basis	Nitrogen As Is Basis	Hide Substance Dry Basis	Chrome Oxide Data As Is Basis	Chrome Oxide Data Dry Basis
Laboratory	7-1=6	39.42	4.12	4.0	0.3671	43.24	0.0555	0.6636
Tannery	7-1=6	11.07	114.14	115.6	3.9693	161.13	2.0503	9.0429
Lab x Tan Interaction	6 x 6=36	0.77	1.23	0.917	0.0566	3.06	0.0080	0.0653
Replications	3 x49=147	1.578	0.76	1.369	0.0902	3.34	0.0114	0.0626

Variance Source	Degrees of Freedom	Ash Dry Basis	Retannage Data Dry Basis	Retannage Data H. S. Basis	pH	Grease Melting Point °C.	Thickness Mils	Stitch Tear lb.
Laboratory	7-1=6	0.2042	49.50	347.72	0.2816	10.14	141.86	1466.66
Tannery	7-1=6	13.0747	49.48	483.79	0.5804	60.06	310.70	466.83
Lab x Tan Interaction	6 x 6=36	0.0258	3.07	26.39	0.0110	1.79	6.86	36.2
Replications	3 x49=147	0.0342	3.37	23.77	0.0128	1.06	8.53	43.7

All laboratory and tannery sources of variance are significant unless a 1 in 100 chance has occurred.

MIL-L-3122. Further, the part played by the tannery producing the leather and the laboratory analyzing the leather has been statistically measured.

Table I shows the analyses of variance resulting from a summarization of the data secured in the second, or ten week, study of the problem. This experiment has been planned so that each laboratory had examined each tanner's leather four times in the ten week period. The table results from a row-column with replication analysis of the data[9], and was secured from 196 values for each characteristic.

Tables II through IX are presented to illustrate the significance of the data in Table I for those not familiar with analysis of variance. The data in the body of these tables comprise the sum of the four replication values secured by the seven laboratories on the leather from the seven tanneries. As a measure of the probability that the differences between these sums result from assignable differences due to the laboratories testing the leather and are not the result of chance variations, rank numbers varying from 1 for the lowest value to 7 for the highest value secured on a given tanner's leather by the seven different laboratories have been inserted. Since the rank numbers can range from 1 to 7, it seems obvious that the sum of the rank numbers for any particular laboratory on all seven tanneries would be 28 (the sum of 1 through 7) if the rank numbers result from pure chance. On the other hand, if one of the laboratories consistently secured either high or low values, its rank sum for all seven tanneries would be 49 or 7 respectively. Therefore, the magnitude of the rank sums and their departure from the average rank sum give an indication that certain laboratories are responsible for determinant causes of variability in the analytical data. The test can be made more precise by the application of Friedman's Chi-square test[13] to these rank sums to establish statistically that there are these determinant causes of variability. This test has been applied to the data secured from the seven laboratories, and the probability is given that rank sums of the magnitude found would occur due to pure chance is recorded in Tables II through IX. Since this probability is always less than 1 in 100, it may be concluded that the laboratories have contributed significantly to the variability of the data.

Tables II through IX also present in the right hand columns the rank sums, chi-square values, and probabilities that result when the data are ranked with respect to tanneries. These data indicate that the tanneries are also responsible for variability in the data; this is of course the expected conclusion, since the tanneries do not endeavor to produce identical leather. However, the data have been presented, because they and the laboratory rank sums together tell the same story that is told by the analysis of variance tables in Table I. It is not particularly surprising that the tanneries should contribute to the variability in the data; it is surprising that the laboratory variance should be as large as the tannery variance. Yet, this is true for the

TABLE II

Rank Analysis of Retan Leather Data
Moisture Content – Sum of Four Values

Tannery	Laboratory B		I		Q		P		R		T		U		Tannery Rank Total
F	50.9	3	54.3	6	53.1	5	47.0	2	51.5	4	42.1	1	57.9	7	40.5
M	47.6	5	46.2	4	47.8	6	43.3	2	45.2	3	35.1	1	54.6	7	14.5
N	46.2	4	45.6	3	46.8	5	47.5	6	40.1	2	36.1	1	50.4	7	11
P	48.9	5	47.7	3	48.6	4	49.4	6	45.2	2	39.4	1	56.4	7	26.5
R	48.4	4	53.0	6	46.7	2	49.1	5	47.8	3	39.8	1	53.3	7	25
T	50.9	3	51.4	4	52.1	5	52.3	6	47.5	2	40.4	1	56.4	7	35
W	52.1	5	51.4	4	53.6	6	49.4	2	50.8	3	42.6	1	57.2	7	43.5
RANK TOTAL		29		30		33		29		19		7		49	

Chi-Square of Ranks $= \frac{12}{7x7x8}(29^2 + 30^2 + 33^2 + 29^2 + 19^2 + 7^2 + 49^2) - 3x7x8$

$= 3/98 \times 6482 - 168 = 198.42 - 168 = 30.42$

$X^2 = 28.4$

$P < 0.001$

P(probability of this being due to pure chance) is less than 0.001

Total Ash—Sum of Four Values

Tannery	Laboratory B		I		Q		P		R		T		U		Tannery Rank Total
F	12.39	3.5	12.34	2	12.0	1	12.41	6	12.40	5	12.39	3.5	12.66	7	7
M	14.72	7	14.02	2	13.32	1	14.60	5	14.58	4	14.64	6	14.29	3	24
N	19.11	5	18.59	3	18.15	1	19.35	6	19.37	7	18.47	2	19.09	4	41
P	14.68	7	14.30	4	13.72	1	14.04	2	14.20	3	14.39	5	14.64	6	22
R	13.89	3	14.07	5	13.13	1	14.21	6	14.25	7	13.76	2	14.02	4	17
T	17.22	4.5	16.56	3	16.48	2	17.71	7	16.26	1	17.22	4.5	17.62	6	36
W	19.96	5	19.57	4	18.61	1	19.46	3	20.00	6	19.21	2	20.02	7	49
RANK TOTAL		35		23		8		35		33		25		37	

Chi-Square of Ranks $= \frac{12}{7x7x8}(35^2 + 23^2 + 8^2 + 35^2 + 33^2 + 25^2 + 37^2) - 3x7x8$

$= 3/98 \times 6126 - 168 = 187.53 - 168 = 19.53$ P is less than 0.01

$X^2 = 39.42$

$P < 0.001$

TABLE III

Rank Analysis of Retan Leather Data — Grease – As Is Basis — Sum of 4 Values

Tannery	Laboratory B		I		Q		P		R		T		U		Tannery Rank Total
F	92.1	7	86.8	1	90.3	5	88.7	3	90.8	4	91.9	6	87.9	2	49
M	76.5	4	75.6	3	74.7	2	78.9	6	79.7	7	74.1	1	77.4	5	34.5
N	71.0	4	68.3	1	71.6	5	69.7	2	73.9	7	72.7	6	70.2	3	26
P	78.9	3.5	76.2	1	78.3-	2	80.8	6	81.2	7	78.9	3.5	77.5	5	42
R	70.7	5	65.9	1	69.9	4	67.2	2	68.3	3	71.0	5	72.0	7	18
T	68.2	6	63.1	1	67.3	5	65.0	2	70.1	7	67.2	4	65.8	3	9
W	68.8	4	64.6	1	67.9	3	69.2	5	69.3	6	74.1	7	66.9	2	17.5
Total Rank		33.5		9		26		26		41		33.5		27	

$X^2 = 37.90$

Chi-Square of Rank $= \frac{12}{7x7x8}(33.5^2 + 9^2 + 26^2 + 41^2 + 33.5^2 + 27^2) - 3x7x8$ $P < 0.001$

$= 3/98 \times 6087.5 - 168 = 184.31 - 168 = 16.31$ P less than 0.01

Grease–Dry Basis—Summation of 4 Values

Tannery	Laboratory B		I		Q		P		R		T		U		Tannery Rank Total
F	104.6	7	102.9	3	103.8	5	100.5	1	104.3	6	102.8	2	103.4	4	49
M	86.6	4	85.2	3	84.8	2	88.6	5	89.9	7	81.2	1	89.6	6	35
N	80.4	4	77.2	1	81.2	6	78.8	2	82.0	7	80.0	3	80.5	5	24
P	89.8	4	86.4	1	89.0	3	92.2	7	92.0	6	87.5	2	90.2	5	41
R	80.5	6	75.8	1	79.0	4	76.5	2	80.1	5	78.9	3	83.2	7	20
T	78.0	6	72.5	1	76.1	4	74.8	3	79.7	7	74.6	2	76.6	5	8
W	79.2	6	74.1	1	78.4	4	79.1	5	78.3	3	83.5	7	78.1	2	19
Total Rank		37		11		28		25		41		20		34	

$X^2 = 36.93$

Chi-Square of Rank $= \frac{12}{7x7x8}(37^2 + 11^2 + 28^2 + 25^2 + 41^2 + 20^2 + 34^2) - 3x7x8$ $P < 0.001$

$= 3/98 \times 6136 - 168 = 187.84 - 168 = 19.84$ P less than 0.01

TABLE IV

Rank Analysis of Retan Leather Data — Nitrogen Analysis, as Received Basis — Sum of Four

Tannery	Laboratory B	I	Q	P	R	T	U	Tannery Rank Total
F	30.50 6	29.51 4	30.55 7	30.21 5	29.28 2	28.54 1	29.29 3	7
M	32.54 1	33.50 4	34.51 7	33.67 6	32.93 2	33.48 3	33.62 5	35
N	32.49 6	32.10 3	33.86 7	32.21 4	32.29 5	31.50 2	31.31 1	19
P	31.75 3	31.91 4	32.40 5	31.19 1	31.50 2	32.49 7	32.41 6	16
R	33.38 2	34.04 5	34.54 7	34.23 6	33.62 4	32.99 1	33.44 3	39
T	33.46 6	33.27 7	34.25 5	32.52 2	33.03 4	32.45 1	32.60 3	31
W	33.76 3	34.37 5	34.89 7	34.30 4	33.72 2	33.51 1	34.37 6	49
RANK TOTAL	27	32	45	28	21	16	27	

Chi-Square of Ranks $= \frac{12}{7x7x8}(27^2 + 32^2 + 45^2 + 28^2 + 21^2 + 16^2 + 27^2) - 3x7x8$ $X^2 = 38.94$

$= 3/98 \times 5988 - 168 = 183.30 - 168 = 15.30$ P is less than 0.01 $P < 0.001$

Hide Substance, Dry Basis — Sum of Four

Tannery	Laboratory B	I	Q	P	R	T	U	Tannery Rank Total
F	196.8 7	191.8 3	196.7 6	192.3 4	188.9 2	175.6 1	192.6 5	7
M	207.0 2	214.6 5	221.2 7	212.0 4	208.5 3	206.4 1	218.8 6	34
N	207.5 6	203.8 4	215.5 7	204.3 5	201.8 3	195.1 1	201.7 2	20
P	203.2 4	204.2 5	207.2 6	200.0 2	199.4 1	202.5 3	209.1 7	17
R	214.2 3	221.4 7	219.9 6	218.2 5	214.1 2	205.7 1	215.8 4	37
T	215.6 6	214.4 5	220.2 7	203.2 2	210.6 3	202.7 1	213.4 4	32
W	217.4 3	221.7 4	226.5 7	219.9 5	217.0 2	207.5 1	225.3 6	49
Rank Total	31	33	46	27	16	9	34	

Chi-Square of Ranks $= \frac{12}{7x7x8}(31^2 + 33^2 + 46^2 + 27^2 + 16^2 + 9^2 + 34^2) - 3x7x8$ $X^2 = 36.30$

$= 3/98 \times 6388 - 168 = 195.55 - 168 = 27.55$ P is less than 0.001 $P < 0.001$

TABLE V

Rank Analysis of Retan Leather Data — Chrome Oxide, As Is Basis — Sum of 4 values

Tannery	Laboratory B	I	Q	P	R	T	U	Tannery Rank Total
F	8.55 5	8.47 4	8.42 2	8.43 3	8.68 7	8.56 6	8.35 1	10.5
M	9.79 6	8.99 1	9.34 2	9.49 4	9.80 7	9.67 5	9.43 3	21
N	10.56 6	10.44 4	10.37 2	10.40 3	10.75 7	10.49 5	10.36 1	39
P	11.02 7	10.36 3	10.54 4	10.35 2	10.74 6	10.64 5	10.16 1	38
R	9.83 5	9.74 3	9.78 4	9.73 2	10.16 7	9.98 6	9.46 1	28
T	8.55 4	8.51 3	8.35 1.5	8.35 1.5	8.61 5	8.78 6	8.82 7	10.5
W	11.63 6	11.33 3	11.26 2	10.94 1	12.11 7	11.43 4.5	11.43 4.5	49
RANK TOTAL	39	21	17.5	16.5	46	37.5	18.5	

Chi Square of Ranks $= \frac{12}{7x7x8}(39^2 + 21^2 + 17.5^2 + 16.5^2 + 46^2 + 37.5^2 + 18.5^2) - 3x7x8$ $X^2 = 40.51$

$= 3/98 \times 6405 - 168 = 196.07 - 168 = 28.07$ P is less than 0.001 $P < 0.001$

Chrome Oxide, Hide Substance Basis

Tannery	Laboratory B	I	Q	P	R	T	U	Tannery Rank Total
F	20.02 2	20.42 5	20.04 3	19.86 1	21.06 6	21.83 7	20.29 4	22
M	21.52 7	19.12 1.5	19.29 3	20.06 4	21.20 6	20.56 5	19.12 1.5	19
N	23.04 4	23.21 5	21.84 1	22.59 2	23.70 6	23.72 7	22.77 3	38
P	24.82 7	23.17 3	23.16 2	23.62 5	24.31 6	23.35 4	22.62 1	42
R	20.68 5	20.21 3	20.20 2	19.76 1	21.52 6	21.55 7	20.27 4	22
T	18.16 2	18.22 3	17.59 1	18.29 4	18.52 6	19.31 7	18.49 5	7
W	24.35 5	23.49 3	22.99 2	22.71 1	25.55 7	24.64 6	23.70 4	46
RANK TOTAL	32	23.5	14	18	43	43	22.5	

Chi Square of Ranks $= \frac{12}{7x7x8}(32^2 + 23.5^2 + 14^2 + 18^2 + 43^2 + 43^2 + 22.5^2) - 3x7x8$ $X^2 = 37.16$

$= 3/98 \times 6300.50 - 168 = 192.87 - 168 = 24.87$ P less than 0.001 $P < 0.001$

TABLE VI

Rank Analysis of Retan Leather Data — Retannage, Dry Basis — Sum of Four Values

Tannery	Laboratory B		I		Q		P		R		T		U		Tannery Rank Total
F	86.7	2	95.8	6	86.4	1	94.8	5	94.7	4	109.2	7	87.6	3	34
M	91.1	6	86.2	4	81.6	2	83.4	3	87.1	5	97.8	7	77.3	1	17
N	93.1	2	100.8	6	85.1	1	97.8	5	96.9	4	107.4	7	95.7	3	43
P	93.3	3	95.3	6	90.3	2	93.9	4	94.5	5	95.6	7	84.8	1	32
R	91.6	5	90.8	3	87.9	1	92.0	6	91.4	4	101.7	7	89.7	2	30
T	89.3	3	98.8	5	84.8	1	104.4	6	93.5	4	105.7	7	88.5	2	33
W	81.4	3	84.6	6	76.5	2	81.6	4	83.6	5	86.7	7	76.4	1	7
Rank Total		24		36		10		33		31		49		13	

Chi Square of Rank $= \frac{12}{7x7x8}(24^2 + 36^2 + 10^2 + 33^2 + 31^2 + 49^2 + 13^2) - 3x7x8$

$= 3/98 \times 6592 - 168 = 201.79 - 168 = 33.79$ P is less than 0.001

$X^2 = 26.55$

$P < 0.001$

Retannage, Hide Substance Basis — Sum of Four Values

Tannery	Laboratory B		I		Q		P		R		T		U		Tannery Rank Total
F	179.0	2	196.5	5	177.1	1	190.7	4	200.6	6	249.0	7	182.0	3	43
M	177.1	6	160.9	4	148.4	2	157.3	3	167.4	5	190.0	7	141.5	1	16
N	179.6	2	197.9	6	159.7	1	192.1	4	192.3	5	220.9	7	190.5	3	41
P	182.8	3	190.2	5	174.7	2	187.9	4	190.4	7	190.3	6	162.0	1	34
R	167.3	3	167.7	4	160.8	2	171.3	5	172.6	6	198.4	7	158.2	1	24
T	165.8	1	166.9	3	171.6	4	207.2	6	177.6	5	208.6	7	166.3	2	31
W	149.5	4	152.8	5	135.8	2	148.5	2	154.2	6	164.8	7	135.6	1	7
Rank Total		21		32		14		29		40		48		12	

Chi Square of Rank $= \frac{12}{7x7x8}(21^2 + 32^2 + 14^2 + 29^2 + 40^2 + 48^2 + 12^2) - 3x7x8$

$= 3/98 \times 6550 - 168 = 200.51 - 168 = 31.49$ P is less than 0.001

$X^2 = 31.83$

$P < 0.001$

TABLE VII

Rank Analysis of Retan Leather Data — pH of Leather — Sum of Four Measurements

Tannery	Laboratory B	I	Q	P	R	T	U	Tannery Rank Total
F	13.41 3	13.21 2	13.09 1	14.55 7	13.56 4	13.68 5	14.43 6	42
M	13.47 3	13.42 1.5	13.42 1.5	15.03 7	13.96 5	13.78 4	14.03 6	48
N	11.99 2	11.73 1	12.05 3	12.72 6.5	12.44 5	12.21 4	12.72 6.5	7
P	12.73 2	12.14 1	13.26 5	13.57 7	12.95 3	13.17 4	13.31 6	31
R	12.75 2	12.28 1	12.84 3	13.45 7	13.06 5	12.90 4	13.26 6	28
T	12.47 2	12.34 1	12.91 4	13.28 7	12.91 5	12.78 3	13.25 6	23.5
W	12.37 3	12.34 2	12.46 4	13.12 7	12.67 5	12.25 1	12.88 6	16.5
RANK TOTAL	17	9.5	21.5	48.5	32	25	42.5	

$X^2 = 36.61$

Chi Square of Rank $= \frac{12}{7x7x8}(17^2 + 9.5^2 + 21.5^2 + 48.5^2 + 32^2 + 25^2 + 42.5^2) - 3x7x8$ $P < 0.001$

$= 3/98 \times 6649 - 168 = 203.54 - 168 = 35.54$ P is less than 0.001

Grease Melting Point, Degrees Centrigrade — Sum of Four Measurements

Tannery	Laboratory B	I	Q	P	R	T	U	Tannery Rank Total
F	170.4 4	165.4 2	166.6 3	171.4 5	171.5 6	177.0 7	165.0 1	7
M	187.9 6	184.5 3	183.6 2	180.5 1	189.0 7	185.6 5	185.0 4	40
N	176.8 3	174.5 1	178.4 4	179.0 5	180.0 6	181.3 7	176.0 2	15
P	184.9 5	183.4 4	181.1 3	181.0 2	186.0 6	188.9 7	180.0 1	30
R	186.8 6	186.7 5	182.2 2	185.0 3	187.5 7	186.1 4	182.0 1	41
T	186.2 5	181.1 3	190.7 6	178.5 1	184.0 4	193.1 7	179.5 2	29
W	186.4 6	183.9 3	187.2 7	182.0 2	185.5 5	184.4 4	181.5 1	34
RANK TOTAL	35	21	27	19	41	41	12	

$X^2 = 29.51$

Chi Square of Rank $= \frac{12}{7x7x8}(35^2 + 21^2 + 27^2 + 19^2 + 41^2 + 12^2) - 3x7x8$ $P < 0.001$

$= 3/98 \times 6262 - 168 = 191.69 - 168 = 23.69$ P is less than 0.001

TABLE VIII

Rank Analysis of Retan Leathers — Thickness of leathers, in mils — Sum of Four

Tannery	Laboratory B		I		Q		P		R		T		U		Tannery Rank Total
F	325.8	1	350.8	6	356.0	7	346.6	3	349.6	5	336.6	2	348.4	4	8
M	362.4	5	375.0	6	379.6	7	354.0	1	355.2	2	358.4	3	361.2	4	21
N	356.6	1	376.4	5	385.9	7	358.4	2	377.8	6	373.0	4	370.6	3	30
P	366.5	2	388.6	6.5	388.6	6.5	365.3	1	383.6	5	372.8	3	383.4	4	41.5
R	373.4	1	380.8	3	406.2	7	375.3	2	390.6	6	383.4	5	383.0	4	46
T	351.4	1	362.8	6	377.4	7	353.2	2	358.4	4	353.0	3	358.8	5	14
W	364.6	3	379.8	5	388.8	7	358.8	1	371.4	4	370.6	3	383.4	6	35.5
RANK TOTAL	13		37.5		48.5		12		32		23		30		

Chi Square of Ranks $= \frac{12}{7x7x8}(13^2 + 37.5^2 + 48.5^2 + 12^2 + 32^2 + 23^2 + 30^2) - 3x7x8$ $X^2 = 37.08$

$= 3/98 \times 6524.50 - 168 = 199.7295 - 168 = 31.7295$ P is less than 0.001 $P < 0.001$

TABLE IX

Rank Analysis — Stitch Tear Strength of Retan Leather — Average of 15 Sides in Pounds

Tannery	Laboratory B		I		Q		P		R		T		U		Tannery Rank Total
1	87.9	6	80.8	4	97.2	7	70.4	1	78.5	3	71.7	2	81.3	5	56
2	84.3	5	85.9	6	92.3	7	73.1	2	77.9	3	66.1	1	83.3	4	51
3	83.3	6	77.2	3	90.4	7	71.3	2	77.6	4	64.3	1	80.5	5	39.5
4	85.7	7	72.9	3	82.0	6	64.6	1	80.7	5	70.2	2	74.2	4	35.5
5	86.1	7	79.3	4	82.0	6	71.3	1	80.4	5	71.9	2	75.5	3	46
6	86.7	7	70.3	4	83.3	6	68.5	3	79.6	5	65.5	2	65.0	1	30
7	82.3	6	68.9	2	89.5	7	75.5	5	74.9	4	67.4	1	70.1	3	32
8	75.6	5	73.2	4	90.0	7	66.7	3	88.7	6	63.7	1	65.4	2	30
9	82.5	6	63.9	1	86.3	7	75.6	4	75.8	5	72.0	3	67.9	2	36
10	87.7	7	71.0	3	83.1	6	75.1	5	73.6	4	62.0	1	65.9	2	29
RANK TOTAL	62		34		66		27		44		16		31		

Chi-Square of Ranks $= \frac{12}{10x7x8}(62^2 + 35^2 + 66^2 + 27^2 + 44^2 + 16^2 + 31^2) - 3x10x8$ $X^2 = 12.64$

$= 3/140 \times 13238 - 240 = 283.67 - 240 = 43.67$ P is less than 0.001 $P < 0.2$

determination of moisture, retannage, and stitch tear, as an examination of the data in Table I will show. Further, in all of the determinations, the laboratory contribution to the variance is so large that it is statistically significant. The laboratories would not contribute this large a variance due to pure chance more than one time in a hundred, hence we may conclude that the laboratories, as well as the tanneries contribute to the variability of analytical data secured on retan leather.

An estimate of the significance of the large error variances (Lab x Tan interaction and replication variance) can be established when the data in Table X are examined. The error variances from Table I have been converted to their square root, the standard deviation. Further, in a second column, the least significant difference[9], which can be detected when two sets of duplicate analyses which show this error variance are compared, is presented. These least significant differences will be exceeded one time out of ten due to chance variations. Hence, any smaller variations are not large enough to be considered significant. Table X presents data of three types. The first results when the same analyst examines the same sample in duplicate at the same time. The second type results when split samples are examined by different analysts in different laboratories, but endeavoring to use the same methods. The third type of results is secured when different analysts in different laboratories examine random samples of a commercial tanner's leather. This latter case is of course the type of analyses which result when leather is analyzed by both the tannery and government laboratories in determining the compliance of leather to specification requirements.

As one would expect, the analysts can do very well when they perform duplicate analyses simultaneously on the same leather, as is shown in the first two columns of Table X. On the other hand, when different analysts examine the same leather in different laboratories, the data in the second two columns of Table X show that large errors are encountered. These results suggest that the methods are basically capable of giving good precision, but that they need more exact definition so that the several laboratories use them in exactly the same way. Since the error from random samples is not very much greater than the error on split samples, it seems most probable that the major improvement will result from a study of the details of the use of the methods by the laboratories rather than by any changes of the sampling technique which would require split sample analyses for comparative purposes. That is to say, if the required number of sides is correctly sampled from the correct areas within the sides, the most significant source of error is the lab-oratory doing the testing, not the fact that one laboratory may sample and test one set of sides from a tanner's production while another laboratory samples and tests another set of sides from the same production.

It is of course true that these data were secured from seven laboratories which include, on all of the tests, one or more laboratories which exhibit a

TABLE X

The Precision of Analytical Methods on Retan Leather

Analysis	Basis	Duplicate Analyses — Same Lab at Same Time		Random—Analyses — Split Sample Random Analysts		Random—Analyses — Random Sample Random Analysts	
		Estimated Standard Deviation	Least Significant Difference (P=0.9, n=2)	Estimated Standard Deviation	Least Significant Difference (P=0.9, n=2)	Estimated Standard Deviation	Least Signatificant Difference (P=0.9, n=2)
Moisture – %	As Is	0.25	0.42	1.52	2.53	1.19	1.98
Grease – %	As Is	0.20	0.34	0.70	1.16	1.02	1.70
Grease – %	Dry			0.75	1.25	1.13	1.87
Grease Melting Point	°C.			1.2	2.0	1.1	1.8
Nitrogen – %	As Is	0.045	0.075	0.21	0.35	0.29	0.48
Hide Substance – %	Dry			1.75	2.91	1.81	3.00
Chrome Oxide – %	As Is	0.036	0.060	0.077	0.13	0.11	0.18
Chrome Oxide – %	Hide Subs.			0.23	0.38	0.27	0.45
Total Ash – %	As Is	0.046	0.077				
Total Ash – %	Dry			0.13	0.22	0.18	0.30
Retannage – %	Dry			2.0	3.33	1.82	3.03
Retannage – %	Hide Subs.			4.5	7.5	4.9	8.1
pH	As Is			0.14	0.23	0.35	0.58
Thickness – Av. of 5 Values	Mils					2.86	4.76
Stitch Tear – Ave. of 5 Values	Lb.					6.5	10.8

statistically significant bias in favor of either high or low values. The data have been re-examined after removal of the data from these laboratories showing the extreme values. Since this results in an incomplete set of data which can not be subjected to rigorous statistical analysis, certain assumptions were made. It was decided that, for any particular analysis, all data coming from a laboratory showing a rank sum below 14 or above 42 would be eliminated. In general this eliminated the data of two laboratories in each set of analyses, although in some cases only one laboratory was eliminated. Then, the range of the data between laboratories was re-computed; only those cases where the laboratories had analyzed split samples were used, and the range values were divided into two sets, one coming from two laboratories and one coming from three laboratories. Then, the standard deviation was estimated from the average ranges thus secured and the relationship between range and standard deviation. This relationship, to be found in many statistical textbooks [9] is that the range divided by the standard deviation equals 1.128 where two samples are involved and 1.693 where three samples are involved. These corrected data on the standard deviation of the methods, and the least significant differences between pairs of duplicate analyses appear in Table XI. Although the precision of the methods is improved when data from the laboratories securing the extreme values are eliminated, the error in several of the analyses is still large. Moisture, grease content, hide substance content and pH values are particularly subject to error. Since the retannage figure accumulates the error of the other analyses, its error reflects the error in the other procedures.

TABLE XI

The Precision of Analytical Methods based on Corrected Data. All data from laboratories consistently securing either maximum or minimum values when compared to other laboratories in the set of seven have been eliminated in these calculations

	Basis	Corrected Standard Deviation (Split Sample) (Random Analyst)	Corrected Least Significant Difference (P-0.9, n-2)
Moisture—%	As Is	0.95	1.60
Grease—%	As Is	0.64	1.06
Grease—%	Dry	0.71	1.19
Grease Melting Point	°C.	0.98	1.6
Nitrogen—%	As Is	0.15	0.25
Hide Substance—%	Dry	1.14	1.90
Chrome Oxide—%	As Is	0.07	0.12
Chrome Oxide—%	Hide Substance	0.21	0.35
Total Ash—%	Dry	0.10	0.16
Retannage—%	Dry	1.39	2.31
Retannage—%	Hide Substance	3.65	6.07
pH		0.11	0.19

These data illustrate that study should be made of the methods of analysis to improve their inter-laboratory precision. The hide substance determination is the basis for so many of the chemical characteristics of leather that it seems most imperative to improve it. The A.L.C.A. hide substance sub-committee [15] secured a better precision than is reported in this paper, since the sub-committee range of hide substance values between four laboratories was about 0 .6 per cent, while the range between the five laboratories securing the most precise hide substance values in the analyses reported here was about 1.25 per cent. However, the sub-committee data were secured under ideal conditions, where all samples were weighed out by one analyst, and all laboratories followed detailed, exacting instructions in performing the analyses. On the other hand, the hide substance data reported here were secured by analysts under routine laboratory conditions without the opportunity to follow precise procedural directions. The comparison between the sub-committee results and the data reported here illustrate what can be done in improving the precision of analytical methods by meticulous attention to details. Since hide substance is the basic analysis for all chemical analyses on leather, it seems preferable to study this method to determine how it can be more precisely described so that the laboratories can secure the needed increase in precision.

The accuracy of moisture determination also influences all analyses on leather. This analysis will be variable if the conditioning of the leather is inadequate, as well as if the laboratory method of analysis is inadequate. It would seem necessary to set up experiments to check which source is most significant in establishing the total error secured in these analyses.

The proposal to change the extractor used in the grease determination as recommended by the A.L.C.A. sub-committee on the determination of grease [14] may offer some improvement in the grease analyses. An experiment should be designed to find out the interlaboratory precision of the method and extractor currently used in comparison to the proposed alternate extractor and method.

The pH determination is also subject to considerable error, especially when it is realized that the total pH range found in most leathers is only 2 pH units or less. Some inter-laboratory work on the error in pH determinations has suggested that poisoning of the glass electrode and contamination of the calomel electrode is a major factor in these errors. A requirement that any electrode system show a linear response on three buffers of known pH covering the pH range from 2 to 9 may serve to detect electrode errors sufficiently to minimize the error in pH determinations.

Since the physical data presented are the average of values from five sides, it would seem that they would be fairly well stabilized for variations due to sides. However, the variation due to laboratories is real and significant on thickness, stitch tear, and bursting strength. Calibration of the testing

equipment has been found to be one source of inter-laboratory errors. Different interpretations in the type of equipment permissable under the method causes errors; thus, no data are given in this report on bursting strength, because laboratory interpretation of the method requirement resulted in equipment now known to give different results being used in at least one laboratory. The nature of the bend in the test wire in the stitch tear strength, as well as the exact positioning of the holes are known to be significant factors in establishing the stitch tear strength of a leather. Hence, the physical test methods also need better definition to improve the precision which will result from their use in different laboratories.

Summary

Data have been presented which demonstrate the need for study of the methods commonly used to analyze leather; the goal of this work should be the improvement of the inter-laboratory precision of the methods. As currently used on retan leathers, these methods have such low inter-laboratory precision that differences in the acceptability of a leather in comparison to specification requirements are too probable. This is not due to the inapplicability of statistical sampling procedures to leather, but it is due to some real inter-laboratory errors. These errors are particularly significant in the hide substance, moisture, grease, and pH determinations. Collaborative experiments to determine the cause of these errors is recommended to the American Leather Chemists Association.

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Study of the Burst Test as Applied to Military Upper Leather*†

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Abstracts

For several years the bursting load of leather as measured by the Mullen burst testing machine has been used as a test of one of the physical properties of upper leather. Because of the inability of most of the Mullen testers to burst many types of upper leathers, this tester was replaced at the National Bureau of Standards by a device in which a cylindrical steel plunger with a spherical point was used. By adapting this device to a testing machine with a capacity of 2000 lb., it was possible to burst most specimens of any type of upper leather even with a plunger 1¼ inches in diameter.

A study has just been completed in which different sized plungers were used ranging from 1/32 inch in diameter to 1¼ inches in diameter. The tests were made on a series of different tannages of upper leather. The results of the tests indicate that the bursting load per unit thickness of the leather, P, may be expressed by the formula:

$$P = k (D - a)$$

where D is the diameter of the plunger, expressed in inches; a is a correction related to fiber elasticity; its value was found to be 0.0194 inches; k is a constant characteristic of the average of the lots of leather used in these tests and may be defined as the bursting strength; it is of the order of 12,510, when P is expressed in pounds per inch thickness.

1. Introduction

For over a decade the bursting load of leather as measured by the Mullen burst testing machine has been used as a test of one of the physical properties of upper leather. This machine had generally been associated with the testing of paper. In the burst test, a measure of the strength of the leather is obtained

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in the direction of the minimum stretch while in the tensile test, using dumbbell specimens, a number of tests must be made in both directions of the hide in order to evaluate the strength of the area. Recent work on the strength of upper leather has shown that there is a high degree of correlation between the results of burst and tensile tests made on similar areas of the hide.

Merrill [1] studied the stretching of calf skin by means of the "Mullen" tester. He put special emphasis on the cracking of the grain. Bradley [2] adapted a device for leather which he called the "Lastometer." In this test, a piece of leather is distended by pressure applied to the flesh side by means of a spherical steel ball ½ inch in diameter. The use of the steel ball instead of the hydraulically operated rubber diaphragm was suggested by the fact that the "Mullen" tester, as designed for paper, could not be used on any but light leathers, because sufficient load to break heavy leathers generally broke the diaphragm, also.

Boor and Niedercorn [3] studied the use of the Olsen Burst testing machine for determining the strength of leather. This embodied the Bradley "Lasto-

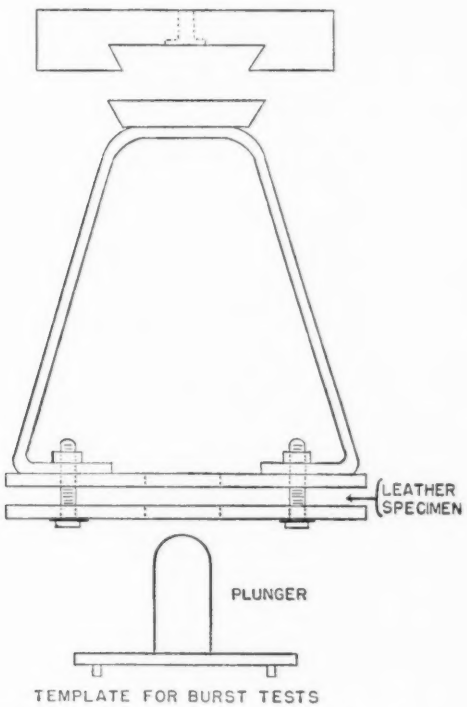

FIGURE 1—Device to hold leather specimen in the burst test.

meter" in principle. Their work with calf skins showed that stresses were produced which closely parallelled those developed during lasting of shoe leather.

During a recent study of the physical properties of shoe upper leather [4] sponsored by the Office of the Quartermaster General, it was found necessary to design apparatus capable of applying loads in excess of those which the Mullen apparatus equipped with a hydraulically loaded rubber diaphragm was able to apply. New apparatus was designed and constructed in which the hydraulically operated rubber diaphragm was replaced by a solid steel plunger. The plunger was mounted on a fixed supporting cradle; the leather specimen was held firmly between two plates (Figure 1). In the original apparatus a plunger, hemispherical at the tip, 2 inches long and 1 inch in diameter, was used with 2 corrugated steel plates having an aperture of 1 3/8

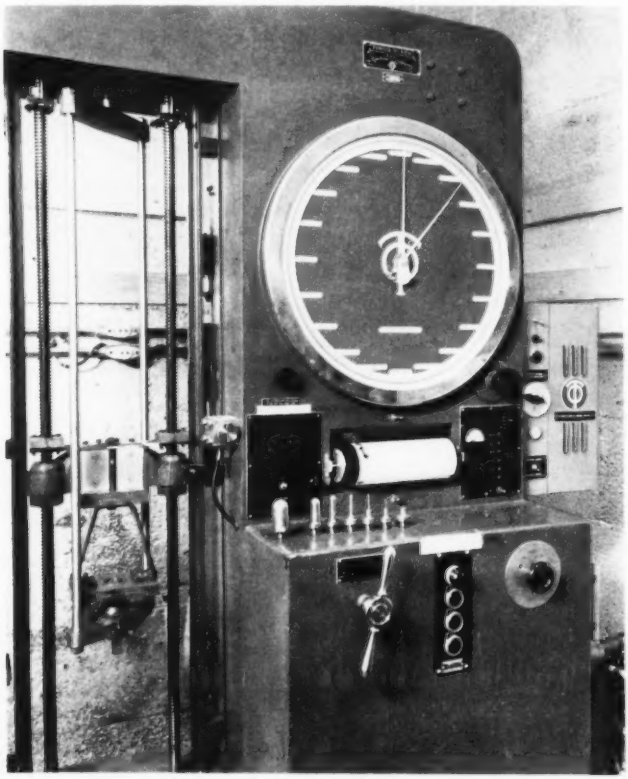

FIGURE 2—The Tinius Olsen machine and the device used for determining the bursting strength.

inches and large enough to accommodate a 4-inch-square specimen. This adapter was used together with an electronically controlled testing machine having a loading capacity of 2000 lb. (Figure 2). Two changes were made to eliminate the tearing of specimens around the edges of the holes in the plates. The edges of the plates around the apertures were beveled and a wooden sleeve was added around the base of the plunger to act as a temporary guide to center the plunger in the hole.

Although satisfactory results were obtained with this adapter, a load of more than 2000 lb. was required to burst some of the leathers. To increase the usefulness of the adapter with this testing machine and other types of testing machines of lower loading capacities, smaller plungers would be needed. It was decided to study the effect of varying the plunger size on

TABLE I

Chemical Analysis of Leathers Used in Study on Bursting Test. Results on Dry Basis.

Lot	Hide Substance	Ash	Cr_2O_3	pH	Grease	Vegetable Tannage
	%	%	%		%	%
			Vegetable			
1	50.8	1.1	——	4.5	16.0	32.1
2	44.6	0.4	——	2.9	24.9	30.1
			Chrome			
3	78.7	5.2	4.7	3.2	8.0	——
4	63.2	4.3	3.9	3.1	26.8	——
			Chrome Retanned, Low Chrome, Low Vegetable			
5	59.8	1.7	1.4	3.2	23.5	15.0
6	56.4	1.7	1.4	3.2	26.5	15.4
7	51.2	1.7	1.3	3.3	30.1	17.0
			Chrome Retanned, Low Chrome, High Vegetable			
8	46.5	1.5	1.1	3.2	23.3	28.7
9	44.5	1.5	1.1	3.2	26.6	27.4
10	42.6	1.4	1.1	3.2	29.6	26.4
			Chrome Retanned, High Chrome, Low Vegetable			
11	48.7	3.8	3.3	3.4	30.8	16.7
12	48.4	3.5	3.1	3.4	34.2	13.9
13	47.2	3.3	2.9	3.2	34.0	15.5
			Chrome Retanned, High Chrome, High Vegetable			
14	50.0	3.7	3.3	3.3	22.1	24.2
15	50.6	3.8	3.2	3.2	23.4	22.2
16	46.5	3.4	3.0	3.2	28.8	21.3
			Chrome Retanned, Low Vegetable, High Chrome			
17	54.0	4.1	3.7	3.3	24.6	17.3
			Reverse Chrome Retanned			
18	45.4	2.4	1.5	3.5	20.6	25.7
			Chrome			
19	75.9	4.3	3.1	3.6	11.1	——

bursting load. Additional plungers of sizes 1/8 inch, 1/4 inch, 1/2 inch, 3/4 inch, and 1 1/4 inches were constructed with plates with holes 3/8 inch larger in diameter than the corresponding plungers. After the results had been obtained with these plungers, plungers 1/16 and 1/32 inch in diameter were constructed and a few experimental results were obtained with them. Since tests with these two smaller plungers were not included in the original statistical plan of the experiment the results are not used in many of the calculations.

2. Preparation and Testing

For the study with the six larger plungers, leathers from six widely varying tannages were chosen. These are shown in Table I and include the lots numbered 1 to 16. Each tannage was represented by different grease, chrome, or vegetable contents giving a total of sixteen lots of leather. The samples consisted of six pieces of leather 12 inches x 8 inches, all cut from the same location of the individual sides so that 96 sides were sampled. The location in the hide from which the pieces were cut corresponds to positions 12 and 13 shown in the paper in the study of the sampling of side upper leather[4]. To eliminate the variability due to the position of the test specimen on a piece and to facilitate the analysis of the data, each 12 inch x 8 inch piece was divided into two rows of three columns of specimens (Figure 3). These six specimens from each of the 96 pieces were tested with the plungers so that for each piece, all six plungers were used once and for each lot all of the six locations were tested once with each of the six plungers. All specimens were tested using the same adapter and testing machine. Only the screw-in plungers and the snap-in plates were changed.

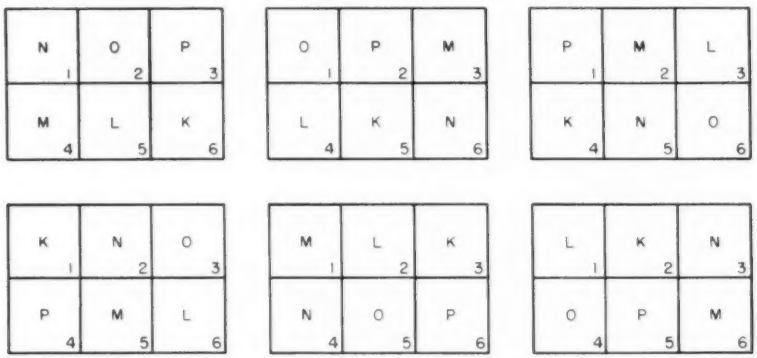
N 1 O 2 P 3
M 4 L 5 K 6
O 1 P 2 M 3
L 4 K 5 N 6
P 1 M 2 L 3
K 4 N 5 O 6
K 1 N 2 O 3
P 4 M 5 L 6
M 1 L 2 K 3
N 4 O 5 P 6
L 1 K 2 N 3
O 4 P 5 M 6
LETTER INDICATES PLUNGER
NUMBER INDICATES SPECIMEN

FIGURE 3—Slecting specimens for the different plungers from the pieces of leather.

All samples were conditioned for one week prior to the preparation of the specimens in an atmosphere of 50 per cent ± 2 per cent relative humidity and at a temperature of 70° ± 2°F. The specimens were prepared and tested under the same conditions. Thicknesses of the specimens were measured to the nearest thousandth of an inch with a dead weight type gage described in Federal Specification KK-L-311. Only one measure of thickness was made on the specimens burst with the five smaller plungers. Thickness of the specimens tested with the three larger plungers was measured in three places over the circular test area and the average value used in subsequent calculations.

TABLE II—PART I

Results of Burst Tests Obtained with 1/32 Inch Diameter Plunger

Lot	Side	Position	Load
			10 lb. / in thick.
4	a	4	13
	b	3	11
	c	1	15
	f	5	13
17	a	1	14
	b	2	16
19	c	4	15
	d	5	15
18	a	5	10
	c	6	13
Average			14

3. Results and Discussion

The results of all the burst tests made are given in Tables II and III. The data are generally expressed in load at burst per unit thickness of leather. The bursting strength is obtained by converting the results to both unit thickness and unit plunger size after applying a correction factor related to the elasticity of the fibers. Data obtained for the plungers of 1/16 and 1/32 inch diameter were placed in a separate table because the experimental work leading to these results was done after completion of the systematic experiment involving the simultaneous study of the larger plungers, of positional effects, and of lot-to-lot variations.

For the purpose of studying the effect of the plunger diameter on the magnitude of the bursting load, the results for all lots were pooled for each of the plungers. The averages are given in Table IV and plotted in Figure 4. From the figure, it appears that the bursting load tends to be proportional to the diameter of the plunger. However, conversion of the data to unit diameter (1 inch) does not lead to constant values except for plunger diameters 1/2 inch

TABLE II—PART 2

Results of Burst Tests Obtained with 1/16 Inch Diameter Plunger

Lot	Side	Position	Load
			10 lb./ in thickness
2	b	5	49
	e	2	38
	f	1	49
			—
Average			45
3	c		56
	f	4	51
			—
Average			54
4	c	5	40
	e	3	30
	f	2	36
			—
Average			35
5	c	6	46
9	d	2	39
	e	1	44
			—
Average			42
14	a	4	44
	b	3	40
	c	2	45
	d	1	48
	e	5	49
	f	6	52
			—
Average			46
12	a	3	39
	b	2	44
	c	1	46
	e	5	42
			—
Average			43
15	a	2	33
	b	1	44
	d	5	55
	e	4	53
	f	3	49
			—
Average			47
Grand Average			44

TABLE III

Results of Burst Tests Made with Different Sized Plungers
Diameter of Plungers: K–⅛″, L–¼″, M–½″, N–¾″, O–1″, P–1¼″
Note: Number in Parenthesis is Position of Specimen in Piece

Plunger	Side a		Side b		Side c		Side d		Side e		Side f		Average
		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness	10 lb/in. thickness
Lot 1													
K	(6)	181	(5)	166	(4)	168	(1)	138	(3)	178	(2)	147	163
L	(5)	313	(4)	323	(3)	376	(6)	276	(2)	314	(1)	282	314
M	(4)	732	(3)	743	(2)	847	(5)	657	(1)	764	(6)	777	753
N	(1)	1214	(6)	1230	(5)	1211	(2)	1032	(4)	1274	(3)	1253	1202
O	(2)	1260	(1)	1139	(6)	1701	(3)	1176	(5)	1617	(4)	1609	1417
P	(3)	1829	(2)	1756	(1)	1938	(4)	1533	(6)	1974	(5)	1932	1827
Average		924		893		1040		802		1020		1000	
Lot 2													
K	(6)	139	(5)	148	(4)	134	(3)	162	(2)	136	(1)	124	140
L	(5)	234	(4)	254	(3)	288	(2)	274	(1)	236	(6)	257	257
M	(4)	540	(3)	743	(2)	583	(1)	573	(6)	655	(5)	556	608
N	(1)	798	(6)	1149	(5)	1129	(4)	1059	(3)	1041	(2)	836	1002
O	(2)	1130	(1)	1363	(6)	1311	(5)	1366	(4)	1020	(3)	1207	1233
P	(3)	1809	(2)	2035	(1)	1512	(6)	1720	(5)	1316	(4)	1245	1606
Average		775		949		853		859		734		704	
Lot 3													
K	(4)	136	(3)	104	(2)	132	(1)	126	(6)	151	(5)	109	126
L	(3)	210	(2)	184	(1)	246	(6)	242	(5)	309	(4)	231	237
M	(2)	435	(1)	285	(6)	485	(5)	577	(4)	590	(3)	436	471
N	(5)	714	(4)	530	(3)	663	(2)	884	(1)	849	(6)	665	717
O	(6)	958	(5)	528	(4)	924	(3)	1009	(2)	905	(1)	708	839
P	(1)	1067	(6)	824	(5)	1183	(4)	1530	(3)	1302	(2)	991	1149
Average		570		409		605		728		684		527	
Lot 4													
K	(1)	122	(6)	117	(5)	131	(4)	114	(3)	117	(2)	67	111
L	(6)	294	(5)	229	(4)	228	(3)	330	(2)	290	(1)	316	281
M	(5)	521	(4)	410	(3)	749	(2)	591	(1)	377	(6)	729	563
N	(2)	946	(1)	512	(6)	1125	(5)	820	(4)	722	(3)	1316	907
O	(3)	1216	(2)	967	(1)	779	(6)	1236	(5)	959	(4)	1309	1119
P	(4)	1522	(3)	1505	(2)	1461	(1)	1210	(6)	1264	(5)	1748	1452
Average		737		623		745		717		621		914	

and greater, and a plot of these converted values (Figure 4) shows a rapid decrease of the ratio of force to diameter with decreasing diameter.

The large diameter plungers give a more nearly constant ratio for the load because a larger percentage of the fibers over the cross section of the plunger necessary to permit penetration are broken. Because of the elasticity of the fibers, the smaller plungers may pass through the leather without breaking all of the fibers encountered in the cross section. This argument is based on

TABLE III

Results of Burst Tests Made with Different Sized Plungers—(Cont'd)
Diameter of Plungers: K-⅛", L-¼", M-½", N-¾", O-1", P-1¼"
Note: Number in Parenthesis is Position of Specimen in Piece

Lot 5

Plunger	Side a		Side b		Side c		Side d		Side e		Side f		Average
	10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness
K	(2)	152	(1)	156	(6)	149	(5)	175	(4)	134	(3)	169	153
L	(1)	261	(6)	299	(5)	336	(4)	358	(3)	298	(2)	399	325
M	(6)	696	(5)	752	(4)	374	(3)	1020	(2)	761	(1)	926	755
N	(3)	1322	(2)	1216	(1)	858	(6)	1949	(5)	1310	(4)	1771	1404
O	(4)	1382	(3)	1176	(2)	1215	(1)	2291	(6)	1111	(5)	2360	1589
P	(5)	2099	(4)	2209	(3)	1342	(2)	2740	(1)	1344	(6)	2148	1980
Average		985		968		712		1422		826		1295	
						Lot 6							
K	(6)	141	(5)	151	(4)	140	(3)	142	(2)	120	(1)	137	138
L	(5)	262	(4)	304	(3)	275	(2)	319	(1)	291	(6)	301	292
M	(4)	491	(3)	725	(2)	605	(1)	623	(6)	663	(5)	617	621
N	(1)	676	(6)	1436	(5)	1131	(4)	828	(3)	840	(2)	933	974
O	(2)	1207	(1)	1454	(6)	1688	(5)	1284	(4)	1146	(3)	1357	1356
P	(3)	1511	(2)	1744	(1)	1253	(6)	1859	(5)	1679	(4)	2500	1758
Average		715		969		849		843		790		974	
						Lot 7							
K	(3)	137	(2)	141	(1)	84	(6)	164	(5)	110	(4)	131	128
L	(2)	251	(1)	351	(6)	193	(5)	294	(4)	181	(3)	252	248
M	(1)	531	(6)	879	(5)	455	(4)	683	(3)	468	(2)	671	614
N	(4)	898	(3)	1313	(2)	581	(1)	654	(6)	810	(5)	1132	898
O	(5)	1253	(4)	1829	(3)	1118	(2)	753	(1)	741	(6)	1265	1160
P	(6)	1626	(5)	2321	(4)	829	(3)	1375	(2)	1017	(1)	1195	1394
Average		734		1133		543		654		555		774	
						Lot 8							
K	(2)	99	(1)	151	(6)	126	(5)	128	(4)	149	(3)	145	133
L	(1)	181	(6)	259	(5)	249	(4)	203	(3)	293	(2)	321	251
M	(6)	432	(5)	740	(4)	419	(3)	567	(2)	730	(1)	633	587
N	(3)	642	(2)	1099	(1)	696	(6)	855	(5)	1304	(4)	1334	988
O	(4)	630	(3)	1145	(2)	902	(1)	869	(6)	1914	(5)	1593	1175
P	(5)	885	(4)	1558	(3)	1103	(2)	1151	(1)	1699	(6)	1756	1359
Average		478		825		583		629		1015		964	

diameter of plunger which theoretically would pass through leather under no measurable load. Note that this takes place not on sound leather but on the assumption that there is sufficient elasticity in the fibers to allow their separation without break by a plunger of sufficiently small diameter.

The application of least squares to the straight line showing the increase in breaking load with increasing plunger diameter (Figure 4) gives a value of 0.0194 inches as the intercept on the diameter of plunger axis. This is the

TABLE III

Results of Burst Tests Made with Different Sized Plungers—(Cont'd)
Diameter of Plungers: K–⅛", L–¼", M–½", N–¾", O–1", P–1¼"
Note: Number in Parenthesis is Position of Specimen in Piece

Lot 9

Plunger	Side a		Side b		Side c		Side d		Side e		Side f		Average
	10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness
K	(5)	149	(4)	117	(3)	102	(2)	93	(1)	100	(6)	164	121
L	(4)	282	(3)	217	(2)	191	(1)	177	(6)	181	(5)	302	225
M	(3)	638	(2)	422	(1)	420	(6)	405	(5)	529	(4)	601	503
N	(6)	1306	(5)	716	(4)	800	(3)	579	(2)	958	(1)	990	892
O	(1)	896	(6)	792	(5)	1094	(4)	910	(3)	635	(2)	1377	951
P	(2)	1676	(1)	1318	(6)	1301	(5)	1148	(4)	986	(3)	1609	1339
Average		825		597		651		555		565		840	
						Lot 10							
K	(3)	115	(2)	130	(1)	88	(6)	154	(5)	135	(4)	104	121
L	(2)	264	(1)	255	(6)	225	(5)	278	(4)	294	(3)	191	251
M	(1)	560	(6)	601	(5)	490	(4)	800	(3)	643	(2)	426	575
N	(4)	946	(3)	947	(2)	739	(1)	953	(6)	974	(5)	764	770
O	(5)	1360	(4)	1372	(3)	728	(2)	1163	(1)	1132	(6)	741	1071
P	(6)	1266	(5)	1874	(4)	1352	(3)	1582	(2)	1475	(1)	906	1493
Average		752		863		604		822		776		522	
						Lot 11							
K	(4)	133	(3)	99	(2)	102	(1)	94	(5)	169	(6)	162	126
L	(3)	185	(2)	226	(1)	182	(6)	225	(4)	401	(5)	425	274
M	(2)	436	(1)	364	(6)	483	(5)	561	(3)	727	(4)	825	566
N	(5)	928	(4)	617	(3)	704	(2)	710	(6)	1178	(1)	1029	861
O	(6)	898	(5)	807	(4)	1141	(3)	983	(1)	1958	(2)	1518	1217
P	(1)	901	(6)	875	(5)	1305	(4)	1243	(2)	1740	(3)	1758	1304
Average		580		498		653		636		1029		953	
						Lot 12							
K	(3)	105	(2)	128	(1)	135	(6)	177	(5)	112	(4)	134	132
L	(2)	251	(1)	298	(6)	283	(5)	380	(4)	265	(3)	302	296
M	(1)	488	(6)	570	(5)	618	(4)	786	(3)	418	(2)	729	603
N	(4)	880	(3)	784	(2)	1031	(1)	1338	(6)	832	(5)	1398	1044
O	(5)	1373	(4)	1501	(3)	988	(2)	1706	(1)	1242	(6)	1590	1400
P	(6)	1250	(5)	1910	(4)	1591	(3)	1927	(2)	982	(1)	1514	1529
Average		724		865		774		1051		642		946	

leather on which the grain is already cracked, since all values for burst are obtained after the grain is ruptured. The slope of this line gives a value of 12510 which is then defined as the average increase in bursting strength per unit thickness of the leathers used in this study when the bursting diameter is increased by 1 inch. It appears, therefore, that the bursting load of leather is a linear function of plunger diameter but not necessarily proportional to it. It approximates the function:

TABLE III

Results of Burst Tests Made with Different Sized Plungers (Cont'd)
Diameter of Plungers: K–⅛", L–¼", M–½", N–¾", O–1", P–1¼"
Note: Number in Parenthesis is Position of Specimen in Piece

Plunger	Side a		Side b		Side c		Side d		Side e		Side f		Average
	10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness		10 lb/in. thickness
					Lot 13								
K	(5)	96	(4)	154	(3)	121	(2)	139	(1)	144	(6)	179	139
L	(4)	198	(3)	298	(2)	255	(1)	358	(6)	323	(5)	395	304
M	(3)	455	(2)	695	(1)	536	(6)	691	(5)	803	(4)	927	684
N	(6)	739	(5)	1270	(4)	1051	(3)	991	(2)	1198	(1)	1222	1079
O	(1)	584	(6)	1141	(5)	1410	(4)	1696	(3)	1228	(2)	1992	1342
P	(2)	1067	(1)	1593	(6)	1842	(5)	1865	(4)	2287	(3)	1918	1762
Average		523		859		869		957		997		1105	
					Lot 14								
K	(4)	95	(3)	152	(2)	136	(1)	141	(6)	136	(5)	94	126
L	(3)	217	(2)	307	(1)	268	(6)	282	(5)	307	(4)	152	255
M	(2)	354	(1)	688	(6)	795	(5)	414	(4)	843	(3)	349	574
N	(5)	685	(4)	1305	(3)	1200	(2)	1134	(1)	1077	(6)	635	1004
O	(6)	898	(5)	1741	(4)	1546	(3)	1137	(2)	1506	(1)	488	1219
P	(1)	1046	(6)	1984	(5)	1834	(4)	1804	(3)	1639	(2)	648	1492
Average		549		1027		963		812		918		394	
					Lot 15								
K	(2)	82	(1)	121	(6)	100	(5)	126	(4)	116	(3)	148	115
L	(1)	194	(6)	301	(5)	245	(4)	272	(3)	232	(2)	301	257
M	(6)	456	(5)	716	(4)	620	(3)	683	(2)	482	(1)	664	603
N	(3)	339	(2)	900	(1)	650	(6)	1122	(5)	618	(4)	1064	770
O	(4)	986	(3)	1670	(2)	962	(1)	811	(6)	1099	(5)	1398	1156
P	(5)	849	(4)	1497	(3)	1218	(2)	1342	(1)	1412	(6)	1744	1344
Average		484		868		633		726		660		886	
					Lot 16								
K	(4)	118	(3)	116	(2)	107	(1)	99	(6)	123	(5)	170	122
L	(3)	199	(2)	290	(1)	219	(6)	213	(5)	320	(4)	385	271
M	(2)	418	(1)	562	(6)	505	(5)	490	(4)	803	(3)	727	584
N	(5)	917	(4)	1170	(3)	690	(2)	834	(1)	1125	(6)	1364	1017
O	(6)	1068	(5)	1295	(4)	1074	(3)	794	(2)	1562	(1)	1553	1224
P	(1)	870	(6)	1629	(5)	1360	(4)	1302	(3)	1564	(2)	2353	1513
Average		598		844		659		622		916		1092	

$$P = k\,(D-a)$$

where P = Bursting load in lb/in thickness
k = A constant characteristic of the leather
D = Plunger diameter in inches
a = 0.0194 inches.

The average value of k for the leathers used in this study is 12510 lb. per inch thickness, per inch of plunger diameter.

TABLE IV

Summary of Results Obtained in the Study of the Burst Test

Size of plunger diameter	Bursting load average for all specimens	Coefficient of variation*	Ratio of bursting load to plunger diameter	k**
in.	10 lb/in. thickness	%	10 lb/in. thickness	10 lb/in. thickness per inch plunger diameter
1/32	13.5	11.6	432	1139
1/16	44.6	12.7	714	1035
1/8	131	16.1	1048	1241
1/4	271	19.7	1084	1175
1/2	605	24.4	1210	1259
3/4	978	25.4	1304	1339
1	1215	28.8	1215	1239
1 1/4	1514	25.0	1211	1230

*These coefficients refer to bursting load and measure the combined effect of experimental error and side-to-side variation within a lot.

**Ratio of bursting load to corrected plunger diameter (cf. equation (1)).

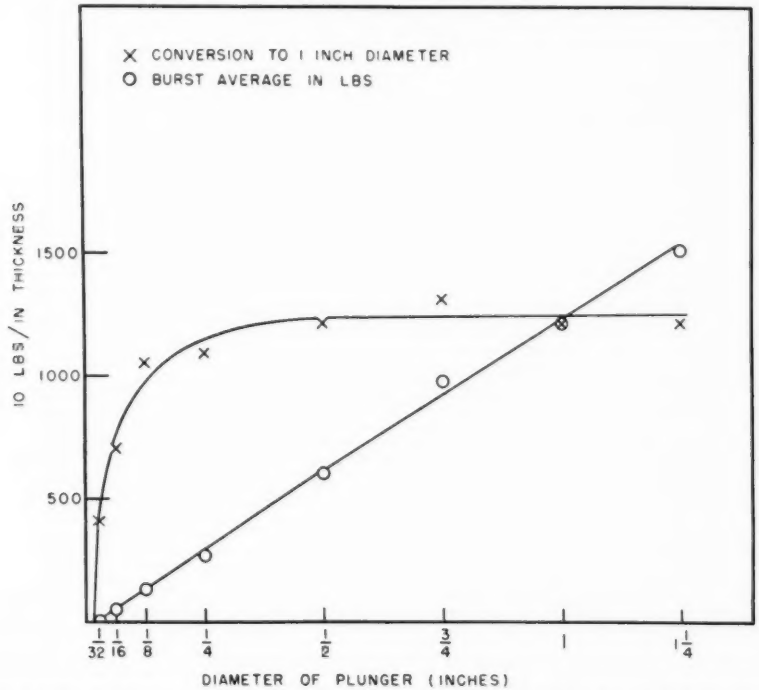

FIGURE 4—Average results obtained for bursting strength with different size plungers expressed directly in pounds and on conversion to 1-inch diameter basis.

The results given in Figure 4, for conversion to unit diameter of plunger without applying the correction factor, show a slight decrease for the plungers 1/4 and 1/8 inches in diameter, and an abrupt decrease for those below 1/8 inch in diameter. On the other hand, the ratios of load to the corrected plunger diameters, i. e., to (D-a), are very nearly the same for all plungers. This suggests that the ratio k may be a more useful measure of bursting strength than the bursting load per unit thickness. It will be shown that there is indeed excellent correlation between the k-values obtained with the different plungers and each of the sixteen lots of leather.

The coefficients of variation listed in Table IV refer to bursting load and were calculated on the basis of analyses of variance [5] performed for the data of each plunger separately. Effects of lot-to-lot variability as well as those due to location on the side are not included in these estimates, which, therefore, are indicative of the combined effects of experimental error and of the variability between sides of the same lot. It is interesting to note that the values obtained with the small plungers while being much smaller than those corresponding to larger plungers, are not subject to proportionally larger errors. In fact, the relative errors for the smaller plungers appear to be smaller than those obtained with the larger plungers.

TABLE V-A

F Values for Plungers Between Positions and Between Lots
Classification by Plungers

Plunger diameter	Between positions	Between lots
1/32	——*	2.48
1/16	——*	2.19
K - 1/8	3.98	2.55
L - 1/4	1.90	1.73
M - 1/2	0.77	1.56
N - 3/4	1.10	2.57
O - 1	1.06	1.65
P - 1 1/4	1.27	2.04

Critical Values of F

Level of significance	Between positions	Between lots		
		Plungers K,L,M,N,O,P.	Plunger 1/32	Plunger 1/2
10%	1.94	1.58	3.29	2.08
5%	2.35	1.82	4.76	2.58
1%	3.30	2.31	9.78	3.84

Before studying the relationship between the results obtained with the different plungers and their sensitivity to variation between lots, it is interesting to determine what effect, if any, the position on the side may have on the value obtained in the plunger test. An analysis of variance, shown in

Table V-A, summarizes these effects for each of the plungers. In examining this and subsequent tables, it may be recalled that an F-value[5], which is considerably larger than unity, indicates the likelihood of a real effect. The critical values for F given in the tables are the largest than can still be attributed to chance fluctuations, on the corresponding levels of significance. The analysis reveals that only for plunger K ($^1/_8$ inch diameter) a positional effect was noticeable. However, even in this case the magnitude of this effect is relatively small with respect to the variability due to the combined effects of experimental error and of differences between sides. The F-values, corresponding to differences between lots, show significant lot-to-lot variations for the results obtained with plungers, K, N, and P. It will be shown, however, that there is general consistency for all plungers in the ranking of the lots.

TABLE V-B

F Values Between Positions and Between Sides
Classification by Lots

Lot	Between positions	Between sides
1	1.56	5.53
2	1.49	2.85
3	1.10	7.82
4	5.16	5.43
5	0.56	4.95
6	2.27	2.63
7	3.45	7.19
8	1.44	8.89
9	1.32	5.82
10	1.58	3.58
11	0.46	7.68
12	1.04	4.28
13	2.17	6.21
14	2.14	9.46
15	0.76	4.71
16	1.18	6.49

Level of significance	Critical value of F
10%	2.16
5%	2.71
1%	4.10

The absence, in general, of positional effects is confirmed by the F-values[5] given in Table V-B which summarizes the results of analysis performed separately on each lot. Only in two of the 16 lots is there a significant effect of position. On the other hand, the analysis by lots shows that in all cases but one, significant differences existed between different sides of the same lot.

The fact that these differences could be detected despite the use of six different plungers for the six specimens tested on each side, suggests already that there is a certain amount of consistency between the various plungers with regard to the results obtained by them on different leather specimens and consequently with regard to lot-to-lot variations.

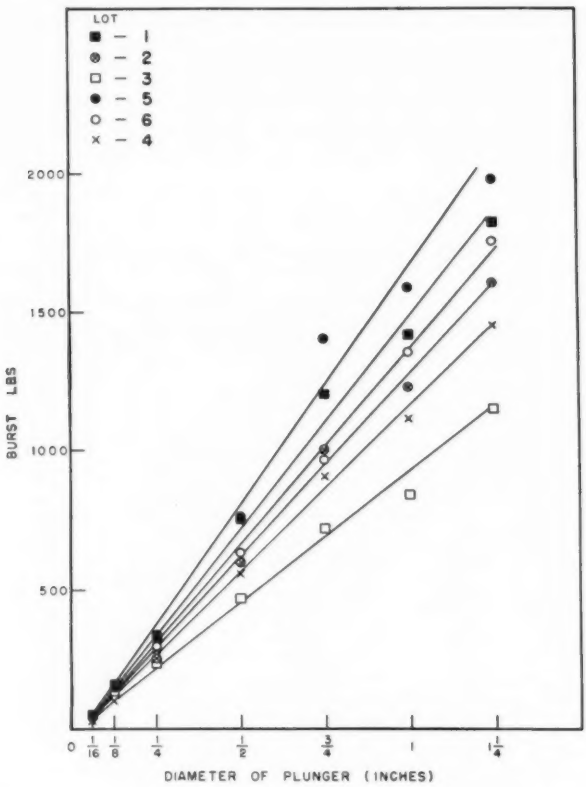

FIGURE 5—Variation of results for some of the lots for different size plungers.

In Figure 5, the average bursting load of some of the lots in pounds per inch in thickness is plotted against size of plunger, and it is seen that lots that have low or high bursting load values with one plunger also tend to have low or high values with all other plungers. Figure 6, which is a plot of the bursting values of all lots for each of 6 plungers also shows the general similarity in the rankings of the lots by all plungers.

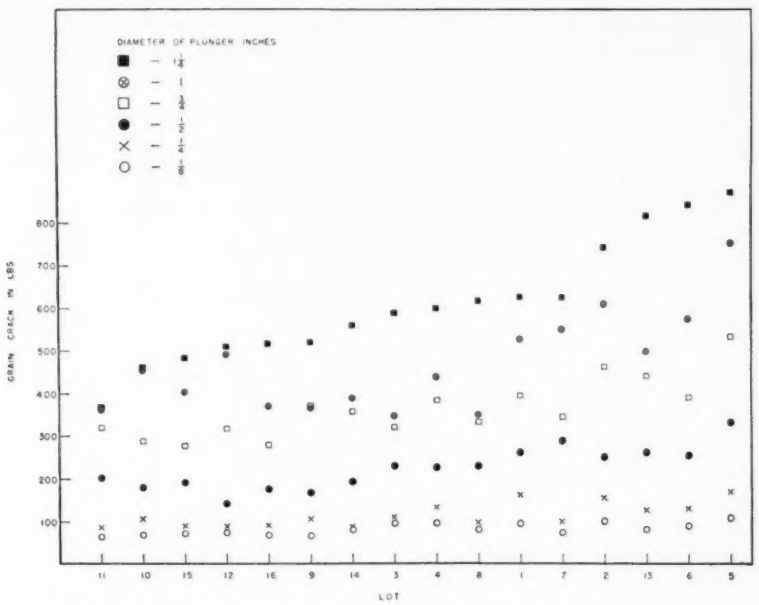

FIGURE 6—Comparison of the results for all lots obtained with different size plungers.

The rankings for the 1/4 and 1/8 inch plungers are obscured in Figure 6 because of the large scale of the graph. A more revealing picture is obtained by ranking the k-values of the lots as they were evaluated by each of the six largest plungers, and also by calculating the correlation coefficient between the results obtained for each of the 6 plungers with the average value for the other five. These results are given in Table VI, and show that all plungers are generally consistent in the ranking of the lots. The 1/8 inch plunger gives the lowest correlation coefficient; however, all of the coefficients are significant beyond the 0.1 per cent level.

The amount of vertical displacement at burst was measured during the burst tests by measuring the amount of plunger travel. The average values are given in column three of Table VII. These values do not correlate with either bursting load, plunger size, or hole size.

A calculation was made of the total elongation of the leather exposed in the hole in the clamp. This was made by estimating the greatest distance from one side, over the top of the cone formed by the plunger, and down over the other side. These figures are given in column five of the table. The percentage of elongation increases from the values obtained with the small 1/8 inch plunger, reaches a maximum with the 3/4 inch plunger and then begins

TABLE VI

Rankings of the Lots of Leather by the Six Largest Plungers and the Correlation Coefficient of each Plunger with Average of other Five.

Lot No.	Size of Plunger						Rank of average
	⅛ in.	¼ in.	½ in.	¾ in.	1 in.	1¼ in.	
1	16	15	15	15	14	15	15
2	14	7½	11	10	10	12	11
3	7	2	1	1	1	1	1
4	1	11	3	7	15	7	9
5	15	16	16	16	16	16	16
6	12	12	13	8	12	13	13
7	9	3	12	6	5	6	6
8	11	4½	8	9	6	5	7
9	3½	1	2	5	2	3	2
10	3½	4½	6	2½	3	8½	4
11	7	10	4	4	7	2	5
12	10	13	9½	13	13	11	12
13	13	14	14	14	11	14	14
14	7	6	5	11	8	8½	8
15	2	7½	9½	2½	4	4	3
16	5	9	7	12	9	10	10
Correlation coefficient	0.751	0.892	0.910	0.890	0.800	0.902	

to drop. The percentage of elongation here is similar in magnitude to that obtained in the tensile test.

A relation of the distention or vertical displacement to the load was given by Bradley:

(2) $h = a\ p^n$ — Where h is the distention, p is the load and a and n are constants. Connecting this equation to the logarithmic form — $\log h = \log a + n \log p$ – where log a is the intercept and n the slope of the curve when log h is plotted against log p. Since it has been found that the dia-

TABLE VII

Elongation of Specimens in Burst Tests

Size of plunger diameter	Size of hole diameter	Vertical displacement		Elongation	
		at burst	at grain crack	at burst	at grain crack
in.	in.	in.	in.	%	%
⅛	½	0.19	0.16	30	24
¼	⅝	0.29	0.20	43	21
½	⅞	0.45	0.29	52	37
¾	1⅛	0.62	0.39	60	38
1	1⅜	0.70	0.43	54	36
1¼	1⅝	0.71	0.48	46	32

meter of the plunger is directly related to the load, it should be possible to use Bradley's equation and substitute diameter for load. The result of this substitution is plotted in Figure 7. The equation for the straight line is – log (distention at burst) = 0.64 log (diameter of plunger) – log 0.147. The logarithm of the distention at burst gives a linear relation with the logarithm of the diameter of the plunger.

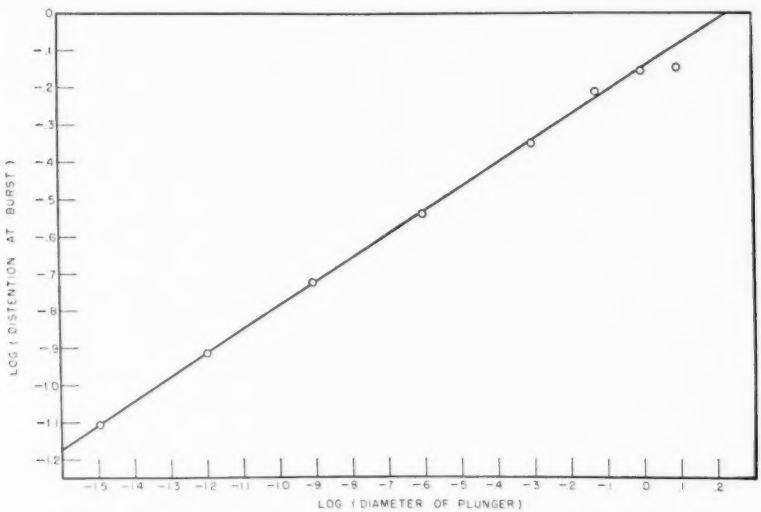

FIGURE 7—Relation between log (distention) and log (diameter of plunger).

The procedure used for determining the bursting load may also be used for determining the load at grain crack. The load at grain crack is an indication of the ability of the leather to withstand the lasting procedure in the shoe factory. The grain crack generally depends upon the stretch of the leather. If the leather is highly stretchy, the grain crack occurs at a low load. Table VIII gives the results obtained in this study for the grain crack of the specimens for each size plunger. These results show that the load required to crack the grain increases as the size of the plunger increases. The results are also shown in Figure 8 where the lots are shown on the x axis arranged according to increase in load at grain crack for the 1 $^1/_4$ inch in diameter plunger. The increase in pounds required for grain crack with increasing size of plunger may be seen more clearly in this figure than in the table.

Vertical displacement and elongation at grain crack are given in columns four and six of Table VII, respectively. It may be noted that the percentage elongation at grain crack reaches the maximum range for the $^1/_2$ inch in

TABLE VIII

Grain Crack of Specimens in Burst Test Study
(Average of 6 Specimens)
Plunger diameter in.

Lot	K-⅛	L-¼	M-½	N-¾	O-1	P-1¼
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
1	97	164	262	397	528	625
2	103	157	253	463	613	743
3	97	111	232	322	347	590
4	97	134	228	386	440	600
5	110	171	333	533	753	870
6	92	132	254	393	575	842
7	76	101	291	345	550	625
8	82	99	231	335	350	618
9	67	107	169	368	367	541
10	69	108	181	288	457	460
11	65	86	202	320	368	367
12	74	91	143	317	492	520
13	83	129	265	442	498	815
14	84	84	194	358	390	560
15	72	91	192	277	405	485
16	70	93	178	280	373	535
Average	84	116	225	364	469	612

diameter plunger. None of the larger plungers show any greater elongation at lower elongations because the angle of bend over the plunger is sharper.

TABLE IX

Ratio of Load at Burst to Load at Grain Crack
Plunger diameter in.

K-⅛	L-¼	M-½	N-¾	O-1	P-1¼
1.57	2.34	2.68	2.69	2.59	2.47

The ratio of burst to grain crack for the plungers is given in Table IX. These results indicate that a different ratio is obtained for different plungers. The small plungers $^1/_8$ and $^1/_4$ inches in diameter, respectively, give a lower ratio than the larger plungers which indicates that as plunger size decreases grain crack approaches more nearly the value for the burst. As shown in Table X all plungers show a good correlation between burst and grain crack.

An analysis of variance was made of the results for grain crack to determine the effects of position and of lot-to-lot variability. The results given in Table XI show the complete absence of any systematic effect of position on grain crack, for the 6 positions used in the experiment. There is little evidence of

TABLE X

Correlation of Burst and Grain Crack
Plunger diameter in.

K-⅛	L- ¼	M-½	N-¾	O-1	P-1¼
0.86	0.82	0.61	0.71	0.72	0.74

TABLE XI

F Values for Analysis of Variance of Grains Crack
Between Positions and Between Lots
Plunger diameter in.

	K- ⅛	L- ¼	M- ½	N- ¾	O-1	P-1 ¼
Positions	0.48	0.85	0.62	0.30	0.40	1.00
Lots	1.63	2.95	1.38	1.05	1.47	1.52

Level of Significance	Critical Values of F	
%	Positions	Lots
10	3.14	1.58
5	4.43	1.82
1	9.18	2.31

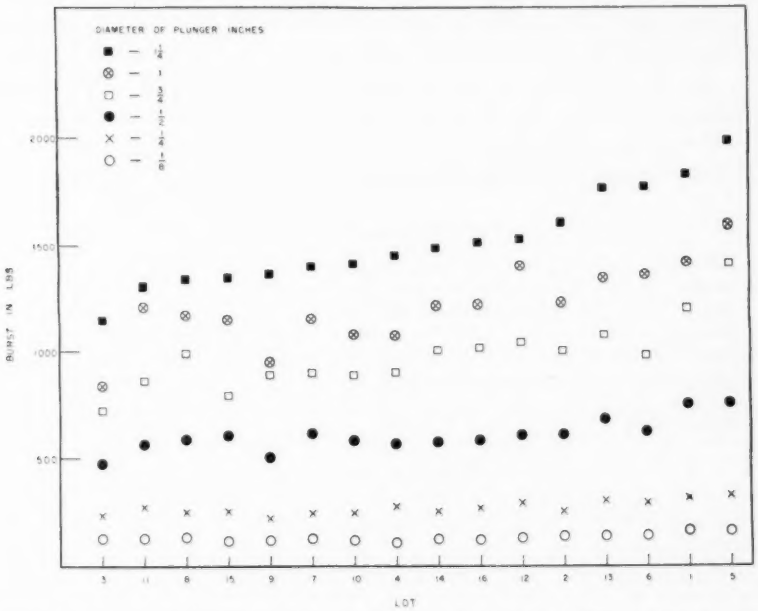

FIGURE 8—Comparison of grain crack for all lots obtained with different size plungers.

lot-to-lot variability for any one plunger, but the fact that for all plungers, the F ratio corresponding to this effect exceeds unity, suggests that relatively slight differences between the lots with respect to grain crack do exist, a result confirmed by examination of Figure 8.

4. Conclusions

The results of the study on the effect of size of plunger in the burst test of leather lead to the following conclusions:

1. The load required to burst leather specimens increases with the diameter of the plunger. For plungers having diameters from 1/2 inch to 1 1/4 inches the ratio of the load to the diameter is approximately the same.

With plungers smaller than 1/2 inch in diameter, the ratio of load to diameter is smaller, and decreases as the diameter decreases.

2. By converting the results to unit thickness and to unit plunger diameter after correcting the latter by a factor related to fiber elasticity, all plungers give approximately the same value for the bursting load. This value is defined as the bursting strength and is given by the formula $K = \frac{P}{D-a}$, where K is the bursting strength; P, the bursting load; D, the diameter of the plunger; and a, the correction related to fiber elasticity. With the use of this formula it will be possible to compare results between laboratories even if they were obtained with different size plungers ranging from 1/8 to 1 1/4 inches in diameter.

3. The relative errors in the bursting load values are not larger for the smaller plungers than for the larger ones, despite the lower burst values obtained with the smaller plungers; and there is satisfactory correlation between the results obtained with the different size plungers on sixteen lots of leather.

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Discussion

I. C. Somerville: What is the effect of the speed of the motion of the plunger?

J. R. Kanagy: We did not make a study of the speed at this time. We ran the plunger at the rate of one inch per minute; but we did not make a study of the speed.

PETER R. BUECHLER: I would like to ask whether Dr. Kanagy has determined any minimum stretch or burst strength which may be all right for satisfactory lasting?

KANAGY: I believe Mr. Mann can give you more information on that than I can.

C. W. MANN: We have some data on military upper leather showing that a grain crack on the Mullen tester of very much below 400 pounds indicates a leather that is very likely to crack in a lasting operation.

We have found good correlation in the results from the $^1/_8$ inch plunger burst tester and the Mullen tester. The adapter with the $^1/_8$ inch plunger proved very satisfactory for measuring rates of deterioration in Quartermaster storage tests. One important advantage of this apparatus not brought out by Dr. Kanagy is the small area required for a test. Only one square inch is needed and the test does not require a cut specimen. We merely insert the 10 x 13 inch storage piece in the machine for each test. In this way repeated tests can be made less than 1 inch apart, thus eliminating most of the variation in different hide areas.

The greater precision of the smaller plungers was demonstrated in the table of coefficients of variation—that is, the standard deviation divided by the mean—which was approximately 25 per cent for the larger plungers as compared with 15 per cent for the $^1/_8$ inch plunger. Furthermore, replicate measurements on the same specimen show a coefficient of variation of only 2 or 3 per cent for the $^1/_8$ inch plunger which shows the advantage of this apparatus for research purposes.

The Use of Carbon Dioxide for Deliming*

By EDWIN E. OCHS

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The deliming and bating of skins constitutes a very important part of leather processing. It was indeed a great and desirable step forward when obnoxious and difficultly controllable natural puers were replaced by manufactured bates. Bates, as we are aware, are enzyme preparations mixed or used in conjunction with various chemicals whose function is to wholly or partially remove lime from skins during bating in their preparation for tanning.

During the transition from puers to bates in manufacturing kid leather, which is an overnight process requiring seventeen to twenty hours, both methods were used in production and it was never felt that the resulting leather obtained with bates was as satisfactory as that obtained with puers.

*Presented at the Forty-Eighth Annual Meeting, Swampscott, Mass., June 2, 1952.

All other stages of manufacture were controlled to be as nearly identical as possible and judgment of the leather was made by an experienced assorter.

While it may appear that we were being unduly critical, it should be borne in mind that we were dealing with black glazed kid on which no pigment was used or any grain snuffed. Being virtually a completely natural grained leather, although glazed, it was not ironed or pressed making observations of deficiencies more easily discernable. Kid skins are comparatively small, therefore cutting value is important. It was particularly in the flank area that it was felt they were not as full or as continuous a part of the rest of the skin as they should be.

Many experiments were run using different enzymes and chemicals in a number of combinations in an effort to obtain identical results using either method.

In the preparation of puers and during their application, evidence of fermentation was always present. Realizing that fermentation is synonymous with carbon dioxide and its presence known and proven by analysis to be in the beginning and at the end of the puering period, it was tried. The results obtained were encouraging—the finished leather was very satisfactory and apparently had fuller flanks. An end product was produced that we felt was comparable to what we were seeking. The greater fullness of the flank area helped to improve the grading of the leather, or at least the selection. A number of factors must of course be taken into consideration when grading leather. In consequence of the results indicated the method was developed to a practical basis and used.

According to the literature, the bating process is one that is not thoroughly understood and we made no attempt to theorize upon what was happening.

Puered skins and bated skins delimed with carbon dioxide are similar in feel, both processes producing a rougher and dryer surface feel than is customary when other deliming chemicals are used. In other respects the skins have similar characteristics to usual bated stock; they are fallen, flaccid, thumb press, air press, and have a doughy feel.

Interest was naturally keen concerning the possible effect of lime blast, however, no such detrimental effect was ever observed. Subsequent processing apparently takes care of the calcium carbonate formed. It might be mentioned here that no calcium is found in the finished leather.

For an identical alkalinity equilibrium in the bating solution more calcium is retained in the skins when carbon dioxide is the neutralizing or deliming agent. In general we find about 0.5 per cent more calcium on the dry basis figured as the oxide after bating with our particular procedure. The increase in some instances amount to 100%.

In effect the carbon dioxide reacts with the calcium hydroxide in the skin first forming insoluble neutral calcium carbonate, and then part of the carbonate is further acted upon to form soluble calcium bicarbonate. In practice all of the calcium hydroxide is neutralized.

Our bating is done at a somewhat lower pH with carbon dioxide. We have chosen 7.5 for the desired end point. This pH is about the optimum for the enzyme action and a point of minimum swelling for the skins. It is obvious in order to always achieve the same end point technique plays an important role just as it does in all other phases of leather processing. To obtain uniform results it is essential that handling of the stock be done in a uniform and thoughtful way. The amount of calcium retained by the skins can be varied, the higher the pH the higher the calcium content, the lower the pH the lower the calcium content. No difficulty has been perceived in achieving a consistently uniform end pH.

The effect of combining other deliming chemicals with the carbon dioxide was studied. Realizing no serious damage would be done to the leather combining usual and accepted deliming agents, virtually all the tests were made on full sized production packs. The conclusions then made were considered to be more reliable than if we had worked with small experimental packs. In our opinion we found nothing that improved upon using carbon dioxide alone and rather it was felt that when other chemicals were combined in the process they reacted with the calcium in the skins first tending then to defeat the purpose of the carbon dioxide.

In application the carbon dioxide may be injected into the bating liquid as the gas, or dry ice may be added directly to either the reel or drum, whichever may be in use. Our skins, intended for black glazed kid, were being bated in 1000 gallon capacity reels. We elected to inject the gas which was obtained from cylinders of liquid carbon dioxide. The bating reels were equipped with half inch pipe that runs across the bottom of the reels full length, having small holes every six or eight inches. Individual needle valves are set to control the flow of gas into each reel at approximately five pounds pressure. Each reel also has a shut off valve. A number of reels were so equipped, all tapping into a central feed pipe. At the source the gas is released from one or more fifty pound capacity cylinders, passed through a manifold that is heated with warm water to prevent freezing, and then through a pressure valve to regulate the flow. The quantity of gas emitted depends upon the number of reels being bated at the same time, five pounds for each one plus ten pounds added to the aggregate. We no longer buy liquid carbon dioxide but instead we purchase dry ice which is put into converters and used as we did the liquid. Dry ice is considerably cheaper.

A number of packs have been bated adding the dry ice directly to the reels with the same result as injecting the gas. Having the necessary pipe lines, we prefer to continue to inject the gas as it is a little more convenient.

The original work, as previously mentioned, was done on skins intended for black glazed leather. The use of carbon dioxide was then extended to all types of kid leather including lining, slipper, colored upper, white, and suede leathers.

Details of actual procedure for the different types of leather will vary but in general for an overnight bate the paddle is started running, the gas injected and the bate, which does not contain any deliming salts, is added. The bating liquid is spot tested with thymol blue indicator and when it ceases to show a blue color, a pH of approximately 8.5, the gas is continued for another ten minutes then shut off. The running of the paddle is continued for the desired length of time without the CO_2 injection. After the first run the skins set for about two hours and then the paddle is again run and CO_2 injected for ten minutes, the temperature being raised at the same time to the desired point. The running is usually continued for a period of time after the desired temperature has been attained and the gas shut off. The pH will then be about 7.0. The following morning it will be about 7.5. The actual weight of CO_2 used will be in approximately a molecular weight equivalent of, for instance, the ammonium salt replaced.

Skins intended for suede leather are bated in a drum for a short period of time. In this instance we simply add dry ice to the drum on an equivalent molecular weight basis to replace the ammonium salts that would ordinarily be used.

Preliminary experiments have been made on heavier hides, such as kip and cow, and analytically we find an increased calcium content in the hides after bating using carbon dioxide. While we completely neutralize all the calcium when bating kid skins, this condition is not generally so on heavier type skins and hides. Further experiments are being made and it may be found that similar advantages, particularly in the flank area, will be achieved. For skins heavier than kid many approaches suggest themselves, such as an extended bating time with the retention of at least the usual amount of calcium in the hides after bating but more of it in a neutral form rather than as the hydroxide.

Carbon dioxide is absolutely safe to use. While it is acid, no acid damage can occur to the stock no matter what the excess may be. Its lowest possible pH is about 5.5 which according to the literature approaches the point of minimum swelling of 5.0.

From an economic standpoint carbon dioxide is cheaper than other deliming salts. In the form of dry ice it costs 3.9 cents a pound, whereas ammonium chloride costs approximately 7 cents a pound and ammonium sulfate 4 cents a pound, at today's market, but only 42% as much CO_2 is required as ammonium chloride and 37% as much as ammonium sulfate.

From the standpoint of availability carbon dioxide is not apt to come into short supply during critical periods as has been our experience with ammonium salts.

In summation, an outline has been given on the use of carbon dioxide for deliming, attempting to show the reasons for desiring to find a new component to be used in the bating process for skins intended for black glazed kid and

also why it was selected to be tried. The outstanding advantage of its use was stated to be particularly an improvement in fullness in the flank area of the finished leather. A general description of the bating procedure with its use was given. Experimenting with other than kid skins was breifly mentioned. Carbon dioxide was shown to be both safe and economical to use and its probable availability in critical times to be an additional advantage.

Discussion

H. B. Merrill: Did I understand you to say that this method gave you a rougher grain?

E. E. Ochs: No, I did not say that. I said a rougher feel during bating, similar to the one if natural puers are used. It would not be as smooth as if ammonium chloride was used, for instance.

A. W. Goetz: You bated to a pH of around seven, I understand?

Ochs: No. We tried to get a pH of 7.5 at the end.

Goetz: It has been found that if you bate during the earlier periods of your bating process at pHs in the vicinity of 9½ and then reduce to about 8 to 8½ you get a much lower grain. It has been the consensus of opinion of some of us that the amount of lime in the skin is essential to the breakdown of some of the proteins immediately under the grain and, therefore, the lower grade.

Ochs: You mean a low grade in the finished leather?

Goetz: Yes, in the finished leather—and a smooth grain.

Ochs: We have not experienced any difficulty with the grain or the grade We feel our grain and grade are satisfactory.

Goetz: What I am saying is just questioning what you said, that the grain has a rougher feel?

Ochs: That is due to the calcium carbonate that is present momentarily.

Goetz: While on the floor I would like to ask this: Do you find in the bating of skins in a drum that is sealed or in a closed paddle that you obtain a better effect of depletion than when you use ammonium salts? Is the CO_2 reaction more complete—than with ammonium salts—where the paddle or drum may prevent the evolution of ammonia gas which reduces normal ammonium deliming?

Ochs: We do bate in a closed paddle and with a drum, and I will say this: That the action is slower than it is with ammonium salts but it is just as effective.

H. G. Turley: I do not have any question, but I want to make an observation. I remember very well that in this same room, at a meeting we had in 1928, John Arthur Wilson gave a paper that contained some surprising observations, to me—that there was just as much lime in the skin after bating as before. He could not say why—until later on it developed that the water used in his particular tannery was hard water. And I think it is very interesting to hear Mr. Ochs today actually using carbon dioxide for deliming.

Of course, this idea is very old, going back to about 1886, but I assume the combination of the deliming with simultaneous enzyme action is the basis of Mr. Ochs' contribution, and I think it very interesting that this matter came up in our meeting in 1928.

ABSTRACTS

Studies on the Reactive Groups of Collagen. Part I. By R. L. Sykes. *J. Soc. Lea. Trades' Chemists*, **36**, 267 (1952). The work deals primarily with modification directed to the ε-amino group of lysine. Samples of official hide powder were subjected to treatment with nitrous acid, 2.4 dinitrofluorbenzene, glyoxylic acid and sodium bromo-acetate. In the first case color changes indicate the possible formation of some nitroso– or diazo– compounds. In the second treatment dinitrophenyl amino acid (DNP acid) is formed.

The HF is neutralized with sodium bicarbonate. The DNP acid is freed by acid hydolysis, isolated chromatographically and determined colorimetrically. The methods used are described. A check on heat shrunk collagen showed no α-DNP amino acids, indicating no terminal amino groups in collagen. Recovery and analysis of the ε-DNP acids indicate that 75-80 per cent of the lysine groups reacted. Pretreatment of hide powder with sodium glyoxylate and formaldehyde at pH 9.3, followed by determination of the free lysine by the DNFB method, indicated that the glyoxylate blocked off about 1/3 of the lysine and the formaldehyde over half. It has been shown that sodium bromo-acetate, using excess MgO as a buffre, will carboxymethylate some amino groups. Hide powder so treated showed that the free glycine, as determined by the DNFB method, was reduced from 0.24 to 0.02 m. moles/g. A method for making titration curves for protein is described. Curves for untreated protein, and treated with nitrous acid, DNFB, sodium glyoxylate and sodium bromo-acetate are shown. Interpretation of the curves is made. R. H. T.

The Fractionation and Paper Chromatography of Black Wattle Extract. By D. G. Roux. *J. Soc. Leather Trades' Chemists*, **36**, 274 (1952). Black wattle extract consists of gums, sugars and polyphenolic tannins. They may be separated by treating a 10 per cent extract with excess ethanol and filtering. A gelatinous precipitate of gum is segregated. Since this gum occludes and retans tannins, it must be dissolved and re-precipitated 4-5 times to get complete separation. The filtrate and washings are distilled under vacuum, with care to exclude oxygen, to remove the alcohol. Thereafter the tannins are precipitated with lead acetate. The sugars remain in solution and may be recovered from the filtrate. The tannins are freed from the lead acetate by treatment with dilute sulfuric acid. An alternate method is to extract the extract chips with 90 per cent ethanol in a Soxhlet apparatus: but this is objectionable in that the continuous boiling may result in further condensation of the tannins. The gums constitute about 8.6 per cent of the extract on a dry basis. Quantitatively hydrolyzed they gave galactose, arabinose, rhamnose and evidence of a uronic acid residue. The sugar from the fresh bark contains only sucrose: but the commercial extract contained sucrose, glucose and fructose, indicating that processing had caused some hydrolysis. The tannins constitute about 70 per cent of the dried extract. For solvent mixtures n–and iso–propanol to water in the ratio of 7:3, tertiary butanol to water in the same ratio, and water saturated tert-amyl alcohol and sec-butanol gave excellent results. Water satu-

rated phenol is the best of the phenolic solvent mixtures and appears superior to most alcohol water mixtures for some purposes. Acetic acid is only necessary when phenolic acids form part of the extract. Ammoniacal silver nitrate diazotized benzidine and ferrous tartrate reagent in the presence of 10 per cent ammonium acetate buffer were found the most effective spraying agents. For two-dimensional study of the tannins preference was given to water saturated sec-butanol for the first direction and water saturated phenol for the second. Methanol is an excellent solvent for the polyphenolic fraction. Methanol extract of fresh bark, which had been oxidized on a water bath, gave a two-dimensional chromatogram similar to that of the commercial extract, while the unoxidized extract gave a chromatogram markedly different. This indicates that the commercial extract is modified by oxidation. The removal of the gum, as described above, is necessary for good results. For one-dimensional chromatography of the tannin fraction n-butanol: acetic: water (4:1:5) gave good separation of three fluorescent areas, R_fs equal .50, .72 and .90 under U.V. light. The first two were bright yellow, the last blue. That of R_f .72 was suspected to be fisetin. This was confirmed by two-dimensional chromatography. Evidence of resorcinol in the meta hydroxy phenols was found. The ortho and meta hydroxy phenols were separated by fractional lead acetate precipitation. In lead salt precipitation incomplete recovery of tannin may result from peptization of the lead salt, if copiously washed with water, and incomplete liberation of the tannin from the lead acetate. The former is avoided by washing the salt with dilute lead acetate, the latter by dropping the pH to a minimum of 1.5 with sulfuric acid. R. H. T.

The Neutral Salt Effect in Chrome Tanning. By K. H. Gustavson. *J. Soc. Leather Trades' Chemists*, **36**, 284 (1952). This is a discussion of a paper by Shuttleworth. [*This Journal*, **47**, 577 (1952)] The statements that "the neutral salt effect is due to reduced accessibility of reactive protein centers caused by the lyophilic character of the salt, and to saturation of minor electrostatic charges responsible for that portion of the chromium fixed by residual valence forces," and "it is generally accepted that high concentrations of neutral salts reduce chromium fixation in tanning" cannot be accepted. Sodium chloride markedly accelerates and increases fixation of chromium by collagen from dilute solutions of basic chromium chloride. Data point to changes in composition and stability of coordinate groups as well as the electro-chemical behaviour to chromium complexes induced by the neutral salt. As an example a table is given showing that the reaction between basic chromium perchlorate is markedly increased by addition of sodium perchlorate. The belief that Wilson's hydration hypothesis satisfactorily explains neutral salt effect on chrome fixation has been disproved. The charge of the chromium complexes is not in itself the governing factor for tanning power, but rather the nature and composition of the groups associated by chromium in the coordinate sphere. The effect of neutral salts is largely due to their effect on the constitution of the chromium complexes. R. H. T.

Note on the Teory of Chrome Tannage. By S. G. Shuttleworth. *J. Soc. Leather Trades' Chemists*, **36**, 296 (1952). This is a comment on Gustavson's discussion of his paper. Shuttleworth points out that the statements questioned by Gustavson are of relatively minor importance and do not invalidate the theories presented. He presents further arguments for his stand. R. H. T.

Paper Chromatography and Tannins. By H. Kilcher. *J. Soc. Leather Trades' Chemists*, **36**, 331 (1952). The procedure used is the Rutter disc technique [*Anal. Chem.* **23**,

398 (1951)] using No. 3 MM filter paper of 18.5 cm. diameter. A radial strip is cut almost to the center and folded downward to make a tail. The filter paper is then placed on a crystallizing dish with the tail dipping into the mobile phase in the bottom of the dish. One drop of the 5 per cent tannin extract to be identified is placed in the center of the filter paper near the base of the tail. The paper is covered with a second crystallizing dish. The mobile phase giving the best results is 40 per cent acetic acid. The acid rises through the tail developing a chromatogram in a circular fashion over the filter paper. Developing time is about 3 hours. A mercury vapor lamp with a nickel oxide glass filter, giving a wave length of 3660 angstroms, is used. Chromatograms for extracts of quebracho, oak bark, wattle, tizers, chestnut, valonia, sumac, myrobalam and spruce are given. With spruce 80 per cent acetic acid was used. The chromatograms had a diameter of about 13.5 cm. Tests were made at room temperature, about 25 degrees C. Quebracho, oak wood, wattle and tizera gave mostly green fluorescence. Chestnut, oak bark, valonia, sumac, myrobalans, Chinese and Alippo galls gave mostly violet. Spruce, which is mostly blue but with two violet zones, might be included in the second group. Chromatograms for the syntans, Irgatan, Tanigan and Synektan made with 80 per cent acetic acid are also given. R. H. T.

Tannage Without Tannin. By P. Saint-Priest. *Revue Tech. des Ind. du Cuir.* **42**, 161 (1950). The first of a series of articles on tannage with resins or plastics. This paper gives a brief history of resin tannage and of the basic idea behind it: that of introducing monomers into the collagen network and of poly- or co-polymerising them, *in situ*, later. The use of products of the reaction between urea and formaldehyde are discussed. Only mono- (I) and dimethylolurea (II) are susceptible of easy polymerisation and the macromolecules produced differ as a result of the different reactivities of the two systems. I polymerises to form chains whereas II forms gels. Mixtures of the two permit of 3-dimensional polymers. The greatest reactivity occurs with II and this is the one most generally used. The simple process of first penetrating the collagen network at neutral pH, followed by acidification to pH 3, leads to considerable difficulties. The tannage obtained is not stable and changes with time so that the leathers become hard and unusable. Wet leathers at acid pH continue to change with a speed which is directly related to the temperature at which they are maintained. It is shown that these changes are characteristic of the reaction between urea and formaldehyde. Experiments were carried out with formic acid as catalyst and varying its amount from 1 per cent to 15 per cent. Also time for polymerisation was varied, the temperature being held at 15°C. For a given acid, the amount used and, in consequence, the pH, controls the speed of the reaction and also the evaluation of the polymer structure. The lower the pH, the greater the tendency for internal dehydration and for the precipitates to be hard; on the other hand a feebly acid pH gives a slower reaction, favors the elimination of water between the molecules of dimethylol urea and gives products which are more plastic. Temperature has a similar action, so that tannages carried out with warmth give more flexible leathers. It is shown that all tannages show a preliminary hardness, this being followed by a stage in which the leather is flexible and, finally, a third, hard, stage is reached. As the speed of the reaction is slowed down (by less acid conditions and higher temperatures), the flexible stage is reached less rapidly but lasts longer and the reaction can therefore be stopped more easily at this desired stage. However, there are practical limits to time of tannage. With formic acid, 5 per cent seems to strike the best balance between time and "zone of usefulness". Other acids behave differently and each requires separate consideration. How the obstacles encountered in the research were overcome, the characteristics of the leathers obtained, and their possibilities, will be given in future articles. A. N. K.

A Study of Some Sulfates of Zirconium. By R. Lasserre. *Bull. de l'Assoc. Francaise des Chim. des Ind. du Cuir.* **12,** 143 (1950). The principal sulfates and basic sulfates of zirconium, whose existence is today certain, were prepared and their thermal decomposition followed by means of the photographic thermobalance of Chenevard. In all cases, the residue was zirconia. Studies were also made of solutions of normal tanning concentration (2.5 per cent ZrO_2), (I), prepared either in the cold or by maintaining for 2 hours at the boil. Potentiometric neutralization curves with soda show the successive formation of basic salts corresponding to the ratio of $Zr(SO_4)_2$ to NaOH. During tests on the basicification of I, using either soda, sodium carbonate or hydrated zirconia, clear liquors of 63° Sch., were obtained, beyond which point the insoluble salt $Zr(SO_4)_2.3Zr(OH)_4.nH_2O$ precipitated. On aging, liquors not made basic, or made basic with hydrated zirconia, gave monoclinic crystals or $5Zr(SO_4)_2.9Zr(OH)_4.40H_2O$; in the presence of sodium sulfate (basicification with NaOH or Na_2CO_3), rhombohedral hexagonal crystals were obtained, to which the forumla $5Zr(SO_4)_2.9Zr(OH).46H_2O$ was attributed. Passage of more dilute solutions (0.25 per cent ZrO_2) through cation-exchange resins showed the presence of non-cationic complexes in boiled solutions whereas solutions prepared cold contained only ionized salts. Since evaporation of a solution of zirconia in zirconium sulfate solutions, in equimolecular quantities, gave a glass of composition $Zr(SO_4)_2.Zr(OH)_4.nH_2O$ and since, in the basicity tests, crystals of $5Zr(SO_4)_2.9Zr(OH)_4.40H_2O$ were obtained in the same liquors, it is thought that one can pass from $Zr(SO_4).NH_2O$ to $5Zr(SO_4).9Zr(OH)_4$ by simple hydrolysis. Consequently, it seems correct to suppose that zirconium sulfate solutions hydrolyze as follows: $n.Zr(OH)_4 + m.Zr(SO_4)_2 + p.H_2O \rightarrow m.Zr(SO_4)_2.nZr(OH)_4.pH_2O$. The obtainment of the basic salt $Zr(SO_4).Zr(OH)_4.nH_2O$ in the glassy state further suggests that, in the first phase of the hydrolysis, the soluble basic salts formed are probably present as large molecules. Studies were also made of the effects of concentration of tanning liquor; of the addition of Na_2SO_4; and of basicification and acidification. Neutralization, either by the use of alkaline salts or by prolonged washing with water, was studied on both cold-prepared and boiled solutions. Tannage was also carried out on skin which had had the free amino- or free carboxyl- groups partially blocked. When the tanning bath does not contain more than 5 per cent Zr_2, on the weight of raw skin, initially (1 per cent on the solution basis), only 0.045 per cent remains after tannage and the liquor can be considered as completely spent. At concns. greater than 5 per cent (skin basis), the ratio ZrO_2/SO_3, (II), increases in the spent bath though that absorbed shows a constant II of about 1.3, even though in the initial bath it was 0.77. The amt. of Zr fixed by the leather increases with increasing concn. of the liquor but the excess Zr in the spent bath increases equally; beyond 10 per cent ZrO_2 (in the initial bath), the increase in amount of ZrO_2 fixed begins to slow down. With 5 per cent ZrO_2 on the skin weight (1 per cent soln) the collagen absorbs about 20 per cent ZrO_2, while at 10 per cent ZrO_2 it absorbs about 36 per cent. Addition of Na_2SO_4 does not change II and only slightly lowers the amount of ZrO_2 fixed. When zirconium sulfate liquors are made basic, ZrO_2 fixed by the skin increases slowly with increasing basicity up to 30° Sch., then falls off. It is at this basicity that the dehydration index is highest—indicating a good tannage. When the basicity is varied from 0° to 50° Sch, and, in consequence, II varies from 0.77 to 1.54, II absorbed by the pelt varies from 1.28 to 1.56, but it is at 50° Sch. where II is approximately the same in the bath and skin, that fixation is weakest. This contrasts with Cr. tannage where the Cr fixed increases with increasing basicity. When the skin was pickled before tannage, there is a slight decrease in the amount of Zr fixed while the ratio of total ZrO_2 absorbed to total SO_3 absorbed is sharply decreased, due to the considerable absorption of H_2SO_4. However, the II absorbed from the tanning bath remains approximately constant and this is true even when the skin contained the 1.1 milli-equivalents of SO_3 which constitutes saturation according to Theis and Jacoby. Acidification of the tanning bath with H_2SO_4 only slightly diminishes the fixation of ZrO_2 while the fixation of acid

increases so that II absorbed decreases. Therefore it is thought that the fixation of Zr and of H_2SO_4 are two unrelated phenomena and that the slight decrease in Zr fixation can be attributed to the physical changes which skin undergoes in acid media. This behaviour of Zr under conditions of increasing acidity clearly differentiates it from tanage with Cr. Neutralization was carried out at pH values from 2 to 10 on pieces of skin tanned in the same bath: it was found that the ZrO_2 fixed remained constant up to pH 7.5–8.0, when the skin became degraded. Curves for resistance to hydrolysis and for index of dehydration show a maximum tannage at pH 4.5 to 5.0. It seems that a certain quantity of SO_4 ions is necessary to provide the best tannage and, from the potentiometric titration curves of $Zr(SO_4)_2$ solutions, it had been noted that a pH of about 4.5 corresponds to the proportion of the basic salt $2ZrO_2SO_3$ (basicity 7.5). Prolonged washing of the tanned leather shows that practically all the SO_4 ions can be removed without affecting the ZrO_2 and that the final product still has the properties of leather. It made no difference whether the 5 per cent ZrO_2 solution, used for tanning, was boiled or made up cold. When the free amino-groups were blocked either by treatment with HNO_2 or with HCHO, II absorbed remained constant. Tannage was also carried out on skin in which the carboxyl groups had been blocked by methylation. Whereas methylation reduced the fixation of Chrome 25 per cent, that of Zr was scarcely affected and this was shown not to be due to hydrolysis of the methyl ester. Tannage was also carried out with chrome followed by Zr retannage, and also tannage with Zr followed by chrome retannage. In neither case was the fixation of Zr affected, so that fixation of Zr cannot be by means of free amino– or free carboxy– groups. From all these studies, the theory is advanced that Zr tannage takes place by hydrogen-bonding between the OH groups of the large molecules of basic Zr sulfate and the peptide network, the reaction being favored by the low pH of the tanning bath which favors distension of the peptide chains. Other types of bonding are not excluded. Such a theory explains the importance of the amount of ZrO_2 fixed and also explains why neither prolonged washing nor neutralization changes the ZrO_2 content or the appearance of the leather. A. N. K.

New Tannery Machinery Throughout the World and Especially in Europe. *Revue Tech. des Ind. du Cuir*, **42**, 170 (1950). A survey of changes in and new types of tanning machinery introduced within recent years. The first portion abstracts an article by A. Brill published in *Das Leder* (1950, pp. 86-95). Among the machines cited is the Whitney (Turner) fleshing machine with electric drive, the motor being placed on the top of the machine, under a protective cover. The Aulson fleshing machine is of similar type to the Whitney but the rubber roll is driven pneumatically. Three motors are used: one to drive the cylinder; another for the hydraulic pump and the third to operate the pull-out rolls. The Stehling setting-out machine has centralized pressure lubrication. Of the various Slocomb machines: pneumatic setting-out and staking machines; the "Prosperity" plating press which is an adaptation of a textile press to the needs of the leather industry. Several Turner machines; a twin cylinder setting-out machine, a 600 mm. buffing machine driven by a 10 H.P. electric motor, the buffing machine "Fulminosa" which automatically removes the dust by means of a blast of compressed air, the shaving-machine "Rapid" whose principal advantage lies in its being equipped with a lever by means of which the pressure may be adjusted at will to get the most out of the thinner parts of the hide. Brill's article concludes with a description of the photoelectric measuring machine which was reviewed in the July issue of *Revue. Tech. des Ind. du Cuir*. The last part of the survey discusses new machines recently marketed by the Italian firm "Rizzi". These all use rotating cylinders and are integrally hydraulic", in which the opening and closing are carried out hydraulically by merely operating a single valve. This permits of reversing the closure at any instant, whereby the operator can avoid damage to the skin in the event of the skin being improperly laid

in. These advantages are not sufficient to give preference to a machine which also requires hydraulic equipment in addition to all the rest of the mechanism. Further, since the pump must operate constantly even though the hydraulic operation occupies only a fraction of the total working time, mechanical efficiency is poor. However, this is not the case with the integrally hydraulic machines which Rizzi produces: here, all the movements of the machine are actuated by the one pump which consumes no more power than the pumps used merely for opening and closing. In the Rizzi machines, a single motor drives the cylinder and the cylinder drives a rotary pump. The flow of oil from this pump passes through a foot-operated valve into a hydraulic cylinder which closes the machine. As the closure is on the point of being completed, the flow is automatically shifted to a hydraulic motor which operates the pull-out rolls (it being noted that the pull-out is not only completely free from vibration but the speed of rotation is continuously regulatable). This company builds not only the machine but also the pump, hydraulic motors, etc., and has therefore been able to simplify the construction, for example: one end of the machine is a box structure and serves as the oil-reservoir for the hydraulic system. Hence the machines are compact, free from encumbrances and easy to keep clean. Further, the use of oil as the source of power creates a system of automatic lubrication and reduces wear to a minimum. It will be realized, too, that by using the flow from the pump at all times, a high degree of mechanical efficiency is obtained. In the setting-out machines, a pedal permits of reversing the operation rapidly, simply and without shock or jerk. In the fleshing machines, the hydraulic motor can be connected with the sharpening mechanism so that sharpening will take place automatically with the reversal of the movement. It can be seen that this type of machine is extremely simple, gives a smoothness of motion unknown with mechanical systems, offers the possibility of continuous speed regulation over a wide range and does away with all the parts of mechanical operation, such as clutches, reversing-gear, etc., etc., which are particularly delicate. Being continuously lubricated, wear is reduced to a minimum. In addition to the above, there is a detailed description of a new measuring machine produced by Rizzi. Instead of using grooved rollers to move the skin and pins or gears for the measurement, the new machine uses a smooth roller to which small, light discs are attached. This avoids the danger of creases and other marks, on the leather, such as the more usual machines are apt to produce. Further, since the actual measurement is made by electrical contacts, all forms of linkage are eliminated, together with the necessity for lubrication and the constant danger of oil spots on the leather. The integrating, and the power required for the indicating dial, are all carried out electrically. Optical projection is used for reading the measurement, and the totalisor can be re-set to zero at any time. The totalisor can be connected to a marking device which will mark the area, the tanner's trademark, etc., onto the skin. The machine is operated like any other but, because of the absence of moving parts, requires less maintenance. The "exploration" of the skin is more minute than usual so that the measurement is more precise. Because of the lack of pressure, it can be used on the most delicate skins without damage. A. N. K.

Compressed Air and the Dew Point. By E. Immendörfer. *Das Leder*, **3**, 132 (1952). Compressed air for spray coating leather should be dried to prevent separation of water and formation of cloudy films when using finishes in organic solvents. From the compressor the air should be passed through a cooler and water separator then through a warm room to warm the air to the original temperature. L. D. C.

Anion Activity—Cation Activity. New Idea for the Technology of Leather Manufacture. By R. Schubert. *Das Leder* **3**, 155 (1952). In tanning, dyeing and fatliquoring

only complicated high molecular compounds are used. The active group may be either anionic or cationic. Anionic and cationic dyes and anionic fatliquors have long been used, but cationic fatliquors are relatively new. Dyes should be designated as anionic or cationic, not as "acid" or "basic". Hide protein is amphoteric. It may bind anions and take a negative charge or cations and take a positive charge. The power of hides to take up ions is limited. If the materials used in tanning, dyeing and fatliquoring all have the same kind of charge the last ones used are taken up very slowly, whereas a material of opposite charge is taken up rapidly. The charges of various tannery materials and the effect of one on the absorption of another is discussed. I. D. C.

Method for the Rapid Determination of Tannin and Tannin Mixtures. By W. Grassmann and E. Zeschitz. *Das Leder*, **3**, 241 (1952). Determination of tannin by the official method is not suitable for control work in small tanneries. Rapid methods for determining tannin have been proposed, but in general are not satisfactory. Basic dyes are absorbed only slightly by pure cellulose, but ordinary cellulose is dyed to some extent. This absorption can be reduced to a minimum by treating the cellulose with the salt of a trivalent metal, such as chromium or aluminum. Methylene blue is taken up very slightly by cellophane before mordanting with tannin but strongly after mordanting. The following method for determining tannin is proposed. Cellophane strips or foils (from Kalle and Co., Wiesbaden-Biebrich) after pretreatment with a dilute aluminum chloride solution and washing with water, are treated, stirring frequently, for 10 minutes with tannin solutions which have been diluted to contain between 0.2 and 1 per cent of tannin. After carefully wiping with filter paper, the foils are stained for 5 minutes in a bath made up of 40 cc. of saturated alcoholic methylene blue solution, 1900 cc. of methyl alcohol and 100 cc. of glacial acetic acid. The dyed foil is washed for 3-5 minutes in a large volume of 5 per cent aqueous, acetic acid solution, then dried by pressing lightly between filter papers. Color transmittance is measured in some type of colorimeter having photoelectric cells. An "Elphor H" photometer has a movable rack which will carry 10 foils. The slit width must be variable from 1 to 5 millimeters. Standard curves must be obtained with materials that have been analyzed by the hide powder method. By this method no coloration is produced with phenol, pyrocatechol, resorcinol or pyrogallol. The extinction coefficient of gallic acid, in 1 per cent solution, is 0.095; of tannic acid, 0.30; and of sumac extract, 0.25. Instead of methylene blue, iron salts (ferric) may be used for developing the color. In this case the tannin-treated foil should be immersed for 5 minutes in 80 cc. of a solution containing 10 grams of iron alum and 30 cc. of hydrochloric acid per liter, after which it should be washed with a liberal supply of cold water, then dried with filter paper. The color varies with the type of tannin. For example, it is dirty brown with quebracho, mimosa and spruce, blue gray with valonia and chestnut, and intense blue violet with sumac. Intensity of color depends greatly on the concentration of hydrochloric acid and is most intense with no acid. Simple phenols produce no color in this test, and syntans only a trace of color, if any at all. With methylene blue, the color developed with syntans is equal to that with natural tannins. For unknown mixtures the methylene blue method is better because of the uniform color and less divergence in the standard curves. The iron method is useful for determining sumac and if syntans are present. I. D. C.

Leather for Textile Machines. By Victor Meyer-Brehm. *Das Leder* **3**, 251 (1952). The more important types of leathers used in textile machines (except driving belts) and the properties and qualities required of such leathers are briefly described. I. D. C.

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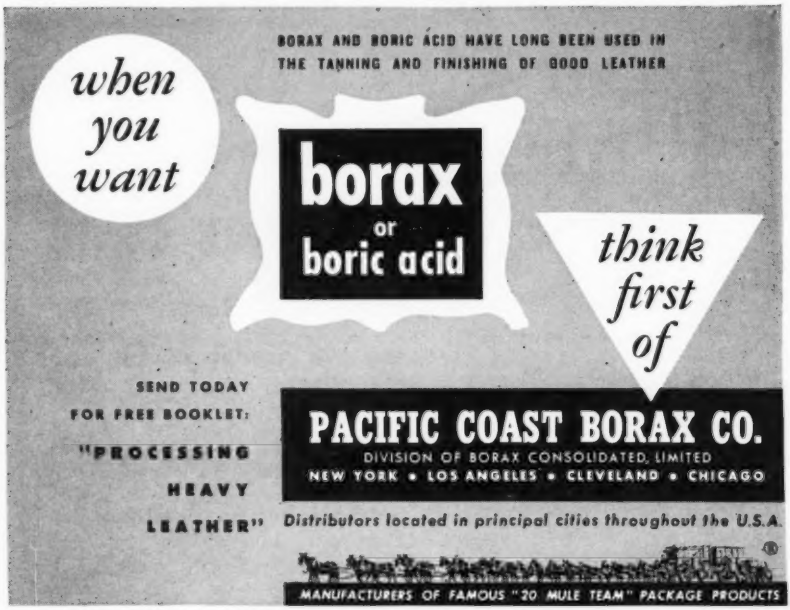
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INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY V
AMERICAN DYEWOOD CO. X
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXV
ARKANSAS COMPANY, INC. VI
ARTHUR C. TRASK CO. XXXIV
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XVI
BARKEY IMPORTING CO., INC. XXXII
BARIUM REDUCTION CORPORATION XXXI
BONA ALLEN, INC. XXVIII
BUCKMAN LABORATORIES, INC. XVII
CHEMTAN COMPANY XXI
EISENDRATH TANNING CO. XXVII
E. F. DREW & CO., INC. XXIX
FRANK F. MARSHALL XXXIV
GARDEN STATE TANNING INC. XXXVII
GARVAMNES AB WEIBULL XXXIX
GENERAL DYESTUFF CORPORATION IX
HOOKER ELECTROCHEMICAL CO. XVIII
HOWES LEATHER CO., INC. XXVIII
INTERNATIONAL PRODUCTS CORP. XII
KEPEC CHEMICAL CORPORATION XXXIV
LEATHER AND SHOES XXXVI
LEATHER MANUFACTURER, THE XXXV
L. H. LINCOLN & SON, INC. XXXIII
MARDEN WILD CORPORATION XXVI
MARTIN DENNIS CO., THE VII
MEAD CORPORATION, THE XIII
MUTUAL CHEMICAL CO. OF AMERICA XXXVIII
NATIONAL ANILINE DIVISION, ALLIED CHEMICAL & DYE CORP. IV
NEWARK LEATHER FINISH CO. XXXV
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PRESTO COLOR CO. XXXVII
REILLY-WHITEMAN-WALTON CO. XXXVII
RIVER PLATE CORPORATION, THE XIV
ROBESON PROCESS CO. II
ROHM & HAAS XV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXVI
SHOE & LEATHER REPORTER XXX
SOCONY-VACUUM OIL CO. I
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XI
SUN OIL COMPANY XXVI
TANEXCO, INC. ..... XL—Inside Back Cover
TANIMEX CORPORATION XXXVIII
TANNERS' COUNCIL RESEARCH LABORATORY XXXVII
TEAS EXTRACT CO. III
UNION STARCH & REFINING CO. XXV
WALLERSTEIN COMPANY, INC. XXIV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXXIV
WOLF, JACQUES & CO. VIII
YOUNG CO., J. S. XX

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INSOLUBLES	.65	.6	.7
WATER	15.98	11.5	6.7
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